THE MECHANICAL THEORY OF HEAT

Rudolf Clausius

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OF
HEAT.

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MECHANICAL THEORY

OF

HEAT.

BY

R. CLAUSIUS.

TRANSLATED BY

WALTER R. BROWNE, M.A.,
LATE FELLOW OF TRINITY COLLEGE, CAMBRIDGE.

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1879

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TRANSLATOR'S PREFACE.

THE following translation was undertaken at the instance of Dr T. Archer Hirst, F.R.S., the translator of the first collected edition (mentioned in the Author's Preface below) of Professor Clausius' papers on the Mechanical Theory of Heat. The former work has however been so completely rewritten by Professor Clausius, that Dr Hirst's translation has been found scarcely anywhere available; and I must therefore accept the full responsibility of the present publication. I trust it may be found to supply a want which I have reason to believe has been felt, namely, that of a systematic and connected treatise on Thermodynamics, for use in Universities and Colleges, and among advanced students generally. With the view of rendering it more complete for this purpose, I have added, with the consent of Professor Clausius, three short appendices on points which he had left unnoticed, but which still seemed of interest, at any rate to English readers. These are, (1) The Thermo-elastic properties of Solids; (2) The application of Thermo-dynamical principles to Capillarity; (3) The Continuity of the Liquid and Gaseous states of Matter. My best thanks are due to Dr John Hopkinson, F.R.S., both for the suggestion of these three points, and also for the original and very elegant investigation from first principles, contained in the first Appendix, and in the commencement of the second. My thanks are also due to Lord Rayleigh, F.R.S., E. J. Routh, Esq., and Professor James Stuart, for kindly looking through the first proof of the translation, and for various valuable suggestions made in connection with it.

WALTER R. BROWNE.

10, VICTORIA CHAMBERS, WESTMINSTER,
November, 1879.

AUTHOR'S PREFACE.

MANY representations having been made to the author from different quarters that the numerous papers "On the Mechanical Theory of Heat," which he had published at different times during a series of years, were inaccessible to many who, from the widespread interest now felt in this theory, were anxious to study them, he undertook some years back to publish a complete collection of his papers relating to the subject.

As a fresh edition of this book has now become necessary, he has determined to give it an entirely new form. The Mechanical Theory of Heat, in its present development, forms already an extensive and independent branch of science. But it is not easy to study such a subject from a series of separate papers, which, having been published at different times, are unconnected in their form, although they agree in their contents. Notes and additions, however freely used to explain and supplement the papers, do not wholly overcome the difficulty. The author, therefore, thought it best so to re-model the papers that they might form a connected whole, and enable the work to become a text-book of the science. He felt himself the more bound to do this because his long experience as a lecturer on the Mechanical Theory of Heat at a Polytechnic School and at several Universities had taught him how the subject-matter should be arranged and represented, so as to render the new view and the new method of calculation adopted in this somewhat difficult theory the more readily intelligible. This plan also enabled him to make use of the investigations of other writers, and by that means to give the subject greater completeness and finish. These authorities of course have been in every case duly recognized by name. During the ten years which have elapsed since the first volume of papers appeared, many fresh investigations into the Mechanical Theory of Heat have been published, and as these have also been discussed, the contents of the volume have been considerably increased.

Therefore in submitting to the public this, the first part of his new investigation of the Mechanical Theory of Heat, the author feels that, although it owes its origin to the second edition of his former volume, still, as it contains so much that is fresh, he may in many respects venture to call it a new work.

R. CLAUSIUS.

BONN, *December*, 1875.

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ON THE MECHANICAL THEORY OF HEAT.

MATHEMATICAL INTRODUCTION.

ON MECHANICAL WORK, ON ENERGY, AND ON THE TREATMENT OF NON-INTEGRABLE DIFFERENTIAL EQUATIONS.

§ 1. *Definition and Measurement of Mechanical Work.*

Every force tends to give motion to the body on which it acts; but it may be prevented from doing so by other opposing forces, so that equilibrium results, and the body remains at rest. In this case the force performs no work. But as soon as the body moves under the influence of the force, Work is performed.

In order to investigate the subject of Work under the simplest possible conditions, we may assume that instead of an extended body the force acts upon a single material point. If this point, which we may call p, travels in the same straight line in which the force tends to move it, then the product of the force and the distance moved through is the mechanical work which the force performs during the motion. If on the other hand the motion of the point is in any other direction than the line of action of the force, then the work performed is represented by the product of the distance moved through, and the component of the force resolved in the direction of motion.

This component of force in the line of motion may be positive or negative in sign, according as it tends in the same direction in which the motion actually takes place, or in the opposite. The work likewise will be positive in the first case, negative in the second. To express the difference in words, which is for many reasons convenient, recourse may be had to a terminology proposed by the writer in a former treatise, and the force may be said to *do* or *perform* work in the former case, and to *destroy* work in the latter.

From the foregoing it is obvious that, to express quantities of work numerically, we should take as unit that quantity of work which is performed by an unit of force acting through an unit of distance. In order to obtain a scale of measurement easy of application, we must choose, as our normal or standard force, some force which is thoroughly known and easy of measurement. The force usually chosen for this purpose is that of gravity.

Gravity acts on a given body as a force always tending downwards, and which for places not too far apart may be taken as absolutely constant. If now we wish to lift a weight upwards by means of any force at our disposal, we must in doing so overcome the force of gravity; and gravity thus gives a measure of the force which we must exert for any slow lifting action. Hence we take as our unit of work that which must be performed in order to lift a unit of weight through a unit of length. The units of weight and length to be chosen are of course matter of indifference; in applied mechanics they are generally the kilogram and the metre respectively, and then the unit of work is called a kilogrammetre. Thus to raise a weight of a kilograms through a height of b metres ab kilogrammetres of work are required; and other quantities of work, in cases where gravity does not come directly into play, can also be expressed in kilogrammetres, by comparing the forces employed with the standard force of gravity.

§ 2. *Mathematical determination of the Work done by variable components of Force.*

In the foregoing explanation it has been tacitly assumed that the active component of force has a constant value throughout the whole of the distance traversed. In reality this is not usually true for a distance of finite length. On first class belong the cases, in which the functions X and Y fulfil the following condition:

$$\frac{dX}{dy} = \frac{dY}{dx} \text{.........................} (4).$$

The second class comprises all cases, in which this condition is not fulfilled.

If the condition (4) is fulfilled, the expression on the right-hand side of equation (3) or (3a) becomes immediately integrable; for it is the complete differential of some function of x and y, in which these may be treated as independent variables, and which is formed from the equations

$$\frac{dF(xy)}{dx} = X, \quad \frac{dF(xy)}{dy} = Y.$$

Thus we obtain at once an equation of the form

$$w = F(xy) + \text{const.} \text{.....................} (5).$$

If condition (4) is not fulfilled, the right-hand side of the equation is not integrable; and it follows that W cannot be expressed as a function of x and y, considered as independent variables. For, if we could put $W = F(xy)$, we should have

$$X = \frac{dW}{dx} = \frac{dF(xy)}{dx},$$

$$Y = \frac{dW}{dy} = \frac{dF(xy)}{dy},$$

whence it follows that

$$\frac{dX}{dy} = \frac{d^2F(xy)}{dxdy},$$

$$\frac{dY}{dx} = \frac{d^2F(xy)}{dydx}.$$

But since with a function of two independent variables the order of differentiation is immaterial, we may put

$$\frac{d^2F(xy)}{dxdy} = \frac{d^2F(xy)}{dydx};$$

whence it follows that $\frac{dX}{dy} = \frac{dY}{dx}$, *i.e.* condition (4) is fulfilled for the functions X and Y; which is contrary to the assumption.

In this case then the integration is impossible, so long as x and y are considered as independent variables. If however we assume any fixed relation to hold between these two quantities, so that one may be expressed as a function of the other, the integration again becomes possible. For if we put

$$f(xy) = 0 \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6),$$

in which f expresses any function whatever, then by means of this equation we can eliminate one of the variables and its differential from the differential equation. (The general form in which equation (6) is given of course comprises the special case in which one of the variables is taken as constant; its differential then becomes zero, and the variable itself only appears as part of the constant coefficient). Supposing y to be the variable eliminated, the equation (3) takes the form $dW = \phi(x)\,dx$, which is a simple differential equation, and gives on integration an equation of the form

$$W = F(x) + \text{const.} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7).$$

The two equations (6) and (7) may thus be treated as forming together a solution of the differential equation. As the form of the function $f(xy)$ may be anything whatever, it is clear that the number of solutions thus to be obtained is infinite.

The form of equation (7) may of course be modified. Thus if we had expressed x in terms of y by means of equation (6), and then eliminated x and dx from the differential equation, this latter would then have taken the form

$$dW = \phi_1(y)\,dy,$$

and on integrating we should have had an equation

$$W = F_1(y) + \text{const.} \ldots\ldots\ldots\ldots\ldots\ldots\ldots(7a).$$

This same equation can be obtained from equation (7) by substituting y for x in that equation by means of equation (6). Or, instead of completely eliminating x from (7), we may prefer a partial elimination. For if the function $F(x)$ contains x several times over in different terms, (and if this does not hold in the original form of the equation, it can be easily introduced into it by writing instead of x an expression such as $(1-a)x+ax$, $\frac{x^{n+1}}{x^n}$, &c.) then it is possible to substitute y for x in some of these expressions, and to let x remain in others. The equation then takes the form

$$W=F_2(x,y)+\text{const.}\qquad\text{(7b)},$$

which is a more general form, embracing the other two as special cases. It is of course understood that the three equations (7), (7*a*), (7*b*), each of which has no meaning except when combined with equation (6), are not different solutions, but different expressions for one and the same solution of the differential equation.

Instead of equation (6), we may also employ, to integrate the differential equation (3), another equation of less simple form, which in addition to the two variables x and y also contains W, and which may itself be a differential equation; the simpler form however suffices for our present purpose, and with this restriction we may sum up the results of this section as follows.

When the condition of immediate integrability, expressed by equation (4), is fulfilled, then we can obtain directly an integral equation of the form:

$$W=F(x,y)+\text{const.}\qquad\text{(A)}.$$

When this condition is not fulfilled, we must first assume some relation between the variables, in order to make integration possible; and we shall thereby obtain a system of two equations of the following form:

$$\left.\begin{aligned}f(x,y)&=0,\\ W&=F(x,y)+\text{const.}\end{aligned}\right\}\qquad\text{(B)},$$

in which the form of the function F depends not only on that of the original differential equation, but also on that of the function f, which may be assumed at pleasure.

§ 4. *Geometrical interpretation of the foregoing results, and observations on partial differential coefficients.*

The important difference between the results in the two cases mentioned above is rendered more clear by treating them geometrically. In so doing we shall for the sake of simplicity assume that the function $F(x, y)$ in equation (A) is such that it has only a single value for any one point in the plane of co-ordinates. We shall also assume that in the movement of the point p its original and final positions are known, and given by the co-ordinates x_0, y_0, and x_1, y_1 respectively. Then in the first case we can find an expression for the work done by the effective force during the motion, without needing to know the actual path traversed. For it is clear, that this work will be expressed, according to condition (A), by the difference $F(x_1y_1) - F(x_0y_0)$. Thus, while the moving point may pass from one position to the other by very different paths, the amount of work done by the force is wholly independent of these, and is completely known as soon as the original and final positions are given.

In the second case it is otherwise. In the system of equations (B), which belongs to this case, the first equation must be treated as the equation to a curve; and (since the form of the second depends upon it) the relation between them may be geometrically expressed by saying that the work done by the effective force during the motion of the point p can only be determined, when the whole of the curve, on which the point moves, is known. If the original and final positions are given, the first equation must indeed be so chosen, that the curve which corresponds to it may pass through those two points; but the number of such possible curves is infinite, and accordingly, in spite of their coincidence at their extremities, they will give an infinite number of possible quantities of work done during the motion.

If we assume that the point p describes a closed curve, so that the final and initial positions coincide, and thus the co-ordinates x_1, y_1 have the same value as x_0, y_0, then in the first case the total work done is equal to zero: in the second case, on the other hand, it need not equal zero, but may have any value positive or negative.

The case here examined also illustrates the fact that a quantity, which cannot be expressed as a function of x and y (so long as these are taken as independent variables), may yet have partial differential coefficients according to x and y, which are expressed by determinate functions of those variables. For it is manifest that, in the strict sense of the words, the components X and Y must be termed the partial differential coefficients of the work W according to x and y: since, when x increases by dx, y remaining constant, the work increases by $X\,dx$; and when y increases by dy, x remaining constant, the work increases by Ydy. Now whether W be a quantity generally expressible as a function of x and y, or one which can only be determined on knowing the path described by the moving point, we may always employ the ordinary notation for the partial differential coefficients of W, and write

$$\left.\begin{aligned}\left(\frac{dW}{dx}\right) &= X,\\ \left(\frac{dW}{dy}\right) &= Y.\end{aligned}\right\}\quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8).$$

Using this notation we may also write the condition (4), the fulfilment or non-fulfilment of which causes the distinction between the two modes of treating the differential equation, in the following form:

$$\frac{d}{dy}\left(\frac{dW}{dx}\right)=\frac{d}{dx}\left(\frac{dW}{dy}\right)\quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9).$$

Thus we may say that the distinction which has to be drawn in reference to the quantity W depends on whether the difference $\frac{d}{dy}\left(\frac{dW}{dx}\right)-\frac{d}{dx}\left(\frac{dW}{dy}\right)$ is equal to zero, or has a finite value.

§ 5. *Extension of the above to three dimensions.*

If the point p be not restricted in its movement to one plane, but left free in space, we then obtain for the element of work an expression very similar to that given in equation (3). Let a, b, c be the cosines of the angles which the direction of the force P, acting on the point, makes with three rectangular axes of co-ordinates; then the three components X, Y, Z of this force will be given by the equations

$$X = aP, \quad Y = bP, \quad Z = cP.$$

Again, let α, β, γ be the cosines of the angles, which the element of space ds makes with the axes; then the three projections dx, dy, dz of this element on those axes are given by the equations

$$dx = \alpha ds, \quad dy = \beta ds, \quad dz = \gamma ds.$$

Hence we have

$$Xdx + Ydy + Zdz = (a\alpha + b\beta + c\gamma) Pds.$$

But if ϕ be the angle between the direction of P and ds, then

$$a\alpha + b\beta + c\gamma = \cos\phi:$$

hence $$Xdx + Ydy + Zdz = \cos\phi \times Pds.$$

Comparing this with equation (2), we obtain

$$dW = Xdx + Ydy + Zdz \text{.................} (10).$$

This is the differential equation for determining the work done. The quantities X, Y, Z may be any functions whatever of the co-ordinates x, y, z; since whatever may be the values of these three components at different points in space, a resultant force P may always be derived from them.

In treating this equation, we must first consider the following three conditions:

$$\frac{dX}{dy} = \frac{dY}{dx}, \quad \frac{dY}{dz} = \frac{dZ}{dy}, \quad \frac{dZ}{dx} = \frac{dX}{dz} \text{............} (11),$$

and must enquire whether or not the functions X, Y, Z satisfy them.

If these three conditions are satisfied, then the expression on the right-hand side of (11) is the complete differential of a function of x, y, z, in which these may all be treated as independent variables. The integration may therefore be at once effected, and we obtain an equation of the form

$$W = F(xyz) + \text{const.} \text{........................} (12).$$

If we now conceive the point p to move from a given initial position (x_0, y_0, z_0) to a given final position (x_1, y_1, z_1) the work done by the force during the motion will be represented by

$$F(x_1, y_1, z_1) - F(x_0, y_0, z_0).$$

If then we suppose $F(x, y, z)$ to be such that it has only a single value for any one point in space, the work will be completely determined by the original and final positions; and it follows that the work done by the force is always the same, whatever path may have been followed by the point in passing from one position to the other.

If the three conditions (1) are not satisfied, the integration cannot be effected in the same general manner. If, however, the path be known in which the motion takes place, the integration becomes thereby possible. If in this case two points are given as the original and final positions, and various curves are conceived as drawn between these points, along any of which the point p may move, then for each of these paths we may obtain a determinate value for the work done; but the values corresponding to these different paths need not be equal, as in the first case, but on the contrary are in general different.

§ 6. *On the Ergal.*

In those cases in which equation (12) holds, or the work done can be simply expressed as a function of the co-ordinates, this function plays a very important part in our calculations. Hamilton gave to it the special name of "force function"; a name applicable also to the more general case where, instead of a single moving point, any number of such points are considered, and where the condition is fulfilled that the work done depends only on the position of the points. In the later and more extended investigations with regard to the quantities which are expressed by this function, it has become needful to introduce a special name for the *negative* value of the function, or in other words for that quantity, the *subtraction* of which gives the work performed; and Rankine proposed for this the term 'potential energy.' This name sets forth very clearly the character of the quantity; but it is somewhat long, and the author has ventured to propose in its place the term "Ergal."

Among the cases in which the force acting on a point has an Ergal, the most prominent is that in which the force originates in attractions or repulsions, exerted on the moving point from fixed points, and the value of which depends only on the distance; in other words the case in which the force may be classed as a central force. Let us take as centre of force a fixed point π, with co-ordinates ξ, η, ζ, and let ρ be its distance from the moving point p, so that

$$\rho = \sqrt{(\xi - x)^2 + (\eta - y)^2 + (\zeta - z)^2} \ldots\ldots\ldots\ldots (13).$$

Let us express the force which π exerts on p by $\phi'(\rho)$, in which a positive value of the function expresses attraction, and a negative value repulsion; we then have for the components of the force the expressions

$$X = \phi'(\rho)\frac{\xi - x}{\rho}; \quad Y = \phi'(\rho)\frac{\eta - y}{\rho}; \quad Z = \phi'(\rho)\frac{\zeta - z}{\rho}.$$

But by (13) $\frac{d\rho}{dx} = -\frac{\xi - x}{\rho}$: hence $X = -\phi'(\rho)\frac{d\rho}{dx}$, and similarly for the other two axes. If $\phi(\rho)$ be a function such that

$$\phi(\rho) = \int \phi'(\rho)\, d\rho \ldots\ldots\ldots\ldots\ldots\ldots (14),$$

we may write the last equation thus:

$$X = -\frac{d\phi(\rho)}{d\rho}\frac{d\rho}{dx} = -\frac{d\phi(\rho)}{dx} \ldots\ldots\ldots\ldots (15),$$

and similarly $Y = -\frac{d\phi(\rho)}{dy}, \quad Z = -\frac{d\phi(\rho)}{dz} \ldots\ldots\ldots (15a).$

Hence we have

$$Xdx + Ydy + Zdz = -\left[\frac{d\phi(\rho)}{dx}dx + \frac{d\phi(\rho)}{dy}dy + \frac{d\phi(\rho)}{dz}dz\right].$$

But, since in the expression for ρ given in equation (13) the quantities x, y, z are the only variables, and $\phi(\rho)$ may therefore be treated as a function of those three quantities, the expression in brackets forms a perfect differential, and we may write:

$$Xdx + Ydy + Zdz = -d\phi(\rho) \ldots\ldots\ldots\ldots (16).$$

The element of work is thus given by the negative differential of $\phi(\rho)$; whence it follows that $\phi(\rho)$ is in this case the Ergal.

Again, instead of a single fixed point, we may have any number of fixed points π_1, π_2, π_3, &c., the distances of which from p are ρ_1, ρ_2, ρ_3, &c., and which exert on it forces $\phi'(\rho_1), \phi'(\rho_2), \phi'(\rho_3)$, &c. Then if, as in equation (14), we assume $\phi_1(\rho), \phi_2(\rho), \phi_3(\rho)$, &c. to be the integrals of the above functions, we obtain, exactly as in equation (15),

$$X = -\frac{d\phi_1(\rho_1)}{dx} - \frac{d\phi_2(\rho_2)}{dx} - \frac{d\phi_3(\rho_3)}{dx} - \ldots$$

$$= -\frac{d}{dx}[\phi_1(\rho_1) + \phi_2(\rho_2) + \phi_3(\rho_3) + \ldots],$$

or $$X = -\frac{d}{dx}\Sigma\,\phi(\rho) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (17).$$

Similarly $$Y = -\frac{d}{dy}\Sigma\,\phi(\rho),\quad Z = -\frac{d}{dz}\Sigma\,\phi(\rho) \ldots\ldots\ldots (17a),$$

whence $$Xdx + Ydy + Zdz = -d\Sigma\,\phi(\rho) \ldots\ldots\ldots (18).$$

Thus the sum $\Sigma\,\phi(\rho)$ is here the Ergal.

§ 7. *General Extension of the foregoing.*

Hitherto we have only considered a single moving point; we will now extend the method to comprise a system composed of any number of moving points, which are in part acted on by external forces, and in part act mutually on each other.

If this whole system makes an indefinitely small movement, the forces acting on any one point, which forces we may conceive as combined into a single resultant, will perform a quantity of work which may be represented by the expression $(Xdx + Ydy + Zdz)$. Hence the sum of all the work done by all the forces acting in the system may be represented by an expression of the form

$$\Sigma\,(Xdx + Ydy + Zdz),$$

in which the summation extends to all the moving points. This complex expression, like the simpler one treated above, may have under certain circumstances the important peculiarity that it is the complete differential of some function of the co-ordinates of all the moving points; in which case we call this function, taken negatively, the Ergal of the whole system. It follows from this that in a finite movement of the system the total work done is simply equal to the difference between the initial and final values of the Ergal; and therefore (assuming that the function which represents the Ergal is such as to have only one value for one position of the points) the work done is completely determined by the initial and final positions of the points, without its being needful to know the paths, by which these have moved from one position to the other.

This state of things, which, it is obvious, simplifies greatly the determination of the work done, occurs when all the forces acting in the system are central forces, which either act upon the moving points from fixed points, or are actions between the moving points themselves.

First, as regards central forces acting from fixed points, we have already discussed their effect for a single moving point; and this discussion will extend also to the motion of the whole system of points, since the quantity of work done in the motion of a number of points is simply equal to the sum of the quantities of work done in the motion of each several point. We can therefore express the part of the Ergal relating to the action of the fixed points, as before, by $\Sigma\,\phi\,(\rho)$, if we only give such an extension to the summation, that it shall comprise not only as many terms as there are fixed points, but as many terms as there are combinations of one fixed and one moving point.

Next as regards the forces acting between the moving points themselves, we will for the present consider only two points p and p', with co-ordinates x, y, z, and x', y', z', respectively. If r be the distance between these points, we have

$$r=\sqrt{(x'-x)^2+(y'-y)^2+(z'-z)^2}\ldots\ldots\ldots(19).$$

We may denote the force which the points exert on each other by $f'(r)$, a positive value being used for attraction, and a negative for repulsion.

Then the components of the force which the point p exerts in this mutual action are

$$f'(r)\frac{x'-x}{r},\ f'(r)\frac{y'-y}{r},\ f'(r)\frac{z'-z}{r};$$

and the components of the opposite force exerted by p' are

$$f'(r)\frac{x-x'}{r},\ f'(r)\frac{y-y'}{r},\ f'(r)\frac{z-z'}{r}.$$

But by (19), differentiating

$$\frac{dr}{dx}=-\frac{x'-x}{r};\ \frac{dr}{dx'}=-\frac{x-x'}{r};$$

so that the components of force in the direction of x may also be written

$$-f'(r)\frac{dr}{dx};\ -f'(r)\frac{dr}{dx'};$$

and if $f(r)$ be a function such that

$$f(r)=\int f'(r)\,dr\ldots\ldots\ldots\ldots\ldots\ldots(20),$$

the foregoing may also be written

$$\frac{-df(r)}{dx};\ \frac{-df(r)}{dx'}.$$

Similarly the components in the direction of y may be written

$$\frac{-df(r)}{dy};\ \frac{-df(r)}{dy'};$$

and those in the direction of z

$$\frac{-df(r)}{dz};\ \frac{-df(r)}{dz'}.$$

That part of the total work done in the indefinitely small motion of the two points, which is due to the two opposite forces arising from their mutual action, may therefore be expressed as follows:

$$-\left[\frac{df(r)}{dx}dx+\frac{df(r)}{dy}dy+\frac{df(r)}{dz}dz+\frac{df(r)}{dx'}dx'+\frac{df(r)}{dy'}dy' \\ +\frac{df(r)}{dz'}dz'\right].$$

But as r depends only on the six quantities x, y, z, x', y', z', and $f(r)$ can therefore be a function of these six quantities only, the expression in brackets is a perfect differential, and the work done, as far as concerns the mutual action between the two points, may be simply expressed by the function

$$-df(r).$$

In the same way may be expressed the work due to the mutual action of every other pair of points; and the total work done by all the forces which the points exert among themselves is expressed by the algebraical sum

$$-df(r)-df(r')-df(r'')-\ldots;$$

or as it may be otherwise written,

$$-d[f(r)+f(r')+f(r'')+\ldots] \text{ or } -d\Sigma f(r);$$

in which the summation must comprise as many terms as there are combinations of moving points, two and two. This sum $\Sigma f(r)$ is then the part of the Ergal relating to the mutual and opposite actions of all the moving points.

If we now finally add the two kinds of forces together, we obtain, for the total work done in the indefinitely small motion of the system of points, the equation

$$\begin{aligned}\Sigma(Xdx+Ydy+Zdz)&=-d\Sigma\phi(\rho)-d\Sigma f(r)\\ &=-d[\Sigma\phi(\rho)+\Sigma f(r)]\ldots\ldots..(21),\end{aligned}$$

whence it follows that the quantity $\Sigma\phi(\rho)+\Sigma f(r)$ is the Ergal of the whole of the forces acting together in the system.

The assumption lying at the root of the foregoing analysis, viz. that central forces are the only ones acting, is of course only one among all the assumptions mathematically possible as to the forces; but it forms a case of peculiar importance, inasmuch as all the forces which occur in nature may apparently be classed as central forces.

§ 8. *Relation between Work and Vis Viva.*

Hitherto we have only considered the forces which act on the points, and the change in position of the points themselves; their masses and their velocities have been left out of account. We will now take these also into consideration.

The equations of motion for a freely moving point of mass m are well known to be as follows:

$$m\frac{d^2x}{dt^2}=X,\quad m\frac{d^2y}{dt^2}=Y,\quad m\frac{d^2z}{dt^2}=Z \text{............}(22).$$

If we multiply these equations respectively by

$$\frac{dx}{dt}dt,\quad \frac{dy}{dt}dt,\quad \frac{dz}{dt}dt,$$

and then add, we obtain

$$m\left(\frac{dx}{dt}\frac{d^2x}{dt^2}+\frac{dy}{dt}\frac{d^2y}{dt^2}+\frac{dz}{dt}\frac{d^2z}{dt^2}\right)dt=\left(X\frac{dx}{dt}+Y\frac{dy}{dt}+Z\frac{dz}{dt}\right)dt \text{...}(23).$$

The left-hand side of this equation may be transformed into

$$\frac{m}{2}\frac{d}{dt}\left[\left(\frac{dx}{dt}\right)^2+\left(\frac{dy}{dt}\right)^2+\left(\frac{dz}{dt}\right)^2\right]dt,$$

or, if v be the velocity of the point,

$$\frac{m}{2}\frac{d(v^2)}{dt}dt=\frac{d\left(\frac{m}{2}v^2\right)}{dt}dt=d\left(\frac{m}{2}v^2\right);$$

and the equation becomes

$$d\left(\frac{m}{2}v^2\right)=\left(X\frac{dx}{dt}+Y\frac{dy}{dt}+Z\frac{dz}{dt}\right)dt \text{...........}(24).$$

If, instead of a single freely moving point, a whole system of freely moving points is considered, we shall have for every point a similar equation to the above; and by summation we shall obtain the following:

$$d\Sigma \frac{m}{2} v^2 = \Sigma \left(X \frac{dx}{dt} + Y \frac{dy}{dt} + Z \frac{dz}{dt}\right) dt \text{............} (25).$$

Now the quantity $\Sigma \frac{m}{2} v^2$ is* the *vis viva* of the whole system of points. If we take a simple expression for the *vis viva*, and put

$$T = \Sigma \frac{m}{2} v^2 \text{............................} (26),$$

then the equation becomes

$$dT = \Sigma \left(X \frac{dx}{dt} + Y \frac{dy}{dt} + Z \frac{dz}{dt}\right) dt \text{............} (27).$$

But the right-hand side of this equation is the expression for the work done during the time dt. Integrate the equation from an initial time t_0 to a time t, and call T_0 the *vis viva* at time t_0: then the resulting equation is

$$T - T_0 = \int_{t_0}^{t} \Sigma \left(X \frac{dx}{dt} + Y \frac{dy}{dt} + Z \frac{dz}{dt}\right) dt \text{...........} (28),$$

the meaning of which may be expressed as follows:

The Work done during any time by the forces acting upon a system is equal to the increase of the Vis Viva *of the system during the same time.*

In this expression a diminution of Vis Viva is of course treated as a negative increase.

It was assumed at the commencement that all the points were moving freely. It may, however, happen that the points are subjected to certain constraints in reference to their motion. They may be so connected with each other that the motion of one point shall in part determine the motion of others; or there may be external constraints, as for instance, if one of the points is compelled to move in a given fixed plane, or on a given fixed curve, whence it will naturally follow that all those points, which are in any connection with it, will also be to some extent constrained in their motion.

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* *Translator's Note.* The *vis viva* of a particle is here defined as half the mass multiplied by the square of the velocity, and not the whole mass, as was formerly the custom.

If these conditions of constraint can be expressed by equations which contain only the co-ordinates of the points, it may be proved, by methods which we will not here consider more closely, that the reactions, which are implicitly comprised in these conditions, perform no work whatever during the motion of the points; and therefore the principle given above, as expressing the relation between Vis Viva and Work done, is true for constrained, as well as for free motion. It is called the *Principle of the Equivalence of Work and Vis Viva.*

§ 9. *On Energy.*

In equation (28), the work done in the time from t_0 to t is expressed by

$$\int_{t_0}^{t}\Sigma\left(X\frac{dx}{dt}+Y\frac{dy}{dt}+Z\frac{dz}{dt}\right)dt,$$

in which t is considered as the only independent variable, and the co-ordinates of the points and the components of the forces are taken as functions of time only. If these functions are known (for which it is requisite that we should know the whole course of the motion of all the points), then the integration is always possible, and the work done can also be determined as a function of the time.

Cases however occur, as we have seen above, in which it is not necessary to express all the quantities as functions of one variable, but where the integration may still be effected, by writing the differential in the form $\Sigma(Xdx+Ydy+Zdz)$, and considering the co-ordinates therein as independent variables. For this it is necessary that this expression should be a perfect differential of some function of the co-ordinates, or in other words the forces acting on the system must have an Ergal. This Ergal, which is the negative value of the above function, we will denote by a single letter. The letter U is generally chosen for this purpose in works on Mechanics: but in the Mechanical Theory of Heat that letter is needed to express another quantity, which will enter as largely into the discussion; we will therefore denote the Ergal by J. Hence we put:

$$\Sigma(Xdx + Ydy + Zdz) = -dJ \qquad (29),$$

whence if J_0 be the value of the Ergal at time t_0, we have:

$$\int_{t_0}^{t} \Sigma(Xdx + Ydy + Zdz) = J_0 - J \qquad (30),$$

which expresses that the work done in any time is equal to the decrease in the Ergal.

If we substitute $J_0 - J$ for the integral in equation (28), we have:

$$T - T_0 = J_0 - J \text{ or } T + J = T_0 + J_0 \qquad (31);$$

whence we have the following principle: *The sum of the Vis Viva and of the Ergal remains constant during the motion.* This sum, which we will denote by the letter U, so that

$$U = T + J \qquad (32),$$

is called the *Energy* of the system; so that the above principle may be more shortly expressed by saying: *The Energy remains constant during the motion.* This principle, which in recent times has received a much more extended application than formerly, and now forms one of the chief foundations of the whole structure of physical philosophy, is known by the name of *The Principle of the Conservation of Energy.*

CHAPTER I.

FIRST MAIN PRINCIPLE OF THE MECHANICAL THEORY OF HEAT, OR PRINCIPLE OF THE EQUIVALENCE OF HEAT AND WORK.

§ 1. *Nature of Heat.*

Until recently it was the generally accepted view that Heat was a special substance, which was present in bodies in greater or less quantity, and which produced thereby their higher or lower temperature; which was also sent forth from bodies, and in that case passed with immense speed through empty space and through such cavities as ponderable bodies contain, in the form of what is called radiant heat. In later days has arisen the other view that Heat is in reality a mode of motion. According to this view, the heat found in bodies and determining their temperature is treated as being a motion of their ponderable atoms, in which motion the ether existing within the bodies may also participate; and radiant heat is looked upon as an undulatory motion propagated in that ether.

It is not proposed here to set forth the facts, experiments, and inferences, through which men have been brought to this altered view on the subject; this would entail a reference here to much which may be better described in its own place during the course of the book. The conformity with experience of the results deduced from this new theory will probably serve better than anything else to establish the foundations of the theory itself.

We will therefore start with the assumption that Heat consists in a motion of the ultimate particles of bodies and of ether, and that the quantity of heat is a measure of the Vis Viva of this motion. The nature of this motion we shall not attempt to determine, but shall merely apply to Heat the principle of the equivalence of Vis Viva and Work, which applies to motion of every kind; and thus establish a principle which may be called the first main Principle of the Mechanical Theory of Heat.

§ 2. *Positive and negative values of Mechanical Work.*

In § 1 of the Introduction the mechanical work done in the movement of a point under the action of a force was defined to be *The product of the distance moved through and of the component of the force resolved in the direction of motion.* The work is thus positive if the component of force in the line of motion lies on the same side of the initial point as the element of motion, and negative if it falls on the opposite side. From this definition of the positive sign of mechanical work follows the principle of the equivalence of Vis Viva and Work, viz. The increase in the Vis Viva is equal to the work done, or equal to the increase in total work.

The question may also be looked at from another point of view. If a material point has once been set in motion, it can continue this movement, on account of its momentum, even if the force acting on it tends in a direction opposite to that of the motion; though its velocity, and therewith its Vis Viva, will of course be diminishing all the time. A material point acted on by gravity for example, if it has received an upward impulse, can continue to move against the force of gravity, although the latter is continually diminishing the velocity given by the impulse. In such a case the work, if considered as work done by the force, is negative. Conversely however we may reckon work as positive in cases where a force is overcome by the momentum of a previously acquired motion, as negative in cases where the point follows the direction of the force. Applying the form of expression introduced in § 1 of the Introduction, in which the distinction between the two opposite directions of the component of force is indicated by different words, we may express the foregoing more simply as follows: we may determine that not the work done, but the work destroyed, by a force shall be reckoned as positive.

On this method of denoting work done, the principle of the equivalence of Vis Viva and Work takes the following form: *The decrease in the Vis Viva is equal to the increase in the Work done,* or *The sum of the Vis Viva and Work done is constant.* This latter form will be found very convenient in what follows.

In the case of such forces as have an Ergal, the meaning of that quantity was defined (in § 6 of the Introduction) in such a manner that we must say, 'The Work done is equal to the *decrease* in the Ergal.' If we use the method of denoting work just described, we must say on the contrary, 'The work done is equal to the *increase* in the Ergal;' and if the constant occurring as one term of the Ergal be determined in a particular way, we may then regard the Ergal as simply an expression for the work done.

§ 3. *Expression for the first Fundamental Principle.*

Having fixed as above what is to be the positive sign for work done, we may now state as follows the first main Principle of the Mechanical Theory of Heat.

In all cases where work is produced by heat, a quantity of heat is consumed proportional to the work done; and inversely, by the expenditure of the same amount of work the same quantity of heat may be produced.

This follows, on the mechanical conception of heat, from the equivalence of Vis Viva and Work, and is named *The Principle of the Equivalence of Heat and Work.*

If heat is consumed, and work thereby produced, we may say that heat has transformed itself into work; and conversely, if work is expended and heat thereby produced, we may say that work has transformed itself into heat. Using this mode of expression, the foregoing principle takes the following form: *Work may transform itself into heat, and heat conversely into work, the quantity of the one bearing always a fixed proportion to that of the other.*

This principle is established by means of many phenomena which have been long recognized, and of late years has been confirmed by so many experiments of different kinds, that we may accept it, apart from the circumstance of its forming a special case of the general mechanical principle of the Conservation of Energy, as being a principle directly derived from experience and observation.

§ 4. *Numerical Relation between Heat and Work.*

While the mechanical principle asserts that the changes in the Vis Viva and in the corresponding Work done are actually *equal* to each other, the principle which expresses the relation between Heat and Work is one of *Proportion* only. The reason is that heat and work are not measured on the same scale. Work is measured by the mechanical unit of the kilogrammetre, whilst the unit of heat, chosen for convenience of measurement, is *That amount of heat which is required to raise one kilogram of water from* 0° *to* 1° (*Centigrade*). Hence the relation existing between heat and work can be one of proportion only, and the numerical value must be specially determined.

If this numerical value is so chosen as to give the work corresponding to an unit of heat, it is called the Mechanical Equivalent of Heat; if on the contrary it gives the heat corresponding to an unit of work, it is called the Thermal Equivalent of Work. We shall denote the former by E, and the latter by $\frac{1}{E}$.

The determination of this numerical value is effected in different ways. It has sometimes been deduced from already existing data, as was first done on correct principles by Mayer (whose method will be further explained hereafter), although, from the imperfection of the then existing data, his result must be admitted not to have been very exact. At other times it has been sought to determine the number by experiments specially made with that view. To the distinguished English physicist Joule must be assigned the credit of having established this value with the greatest circumspection and care. Some of his experiments, as well as determinations carried out at a later date by others, will more properly find their place after the development of the theory; and we will here confine ourselves to stating those of Joule's experiments which are the most readily understood, and at the same time the most certain as to their results.

Joule measured, under various circumstances, the heat generated by friction, and compared it with the work consumed in producing the friction, for which purpose he employed descending weights. As accounts of these experiments are given in many books, they need not here be described; and it will suffice to state the results as given in his paper, published in the *Phil. Trans.* for 1850.

In the first series of experiments, a very extensive one, water was agitated in a vessel by means of a revolving paddle wheel, which was so arranged that the whole quantity of water could not be brought into an equal state of rotation throughout, but the water, after being set in motion, was continually checked by striking against fixed blades, which occasioned numerous eddies, and so produced a large amount of friction. The result, expressed in English measures, is that in order to produce an amount of heat which will raise 1 pound of water through 1 degree Fahrenheit, an amount of work equal to 772·695 foot-pounds must be consumed. In two other series of experiments quicksilver was agitated in the same way, and gave a result of 774·083 foot-pounds. Lastly, in two series of experiments pieces of cast iron were rubbed against each other under quicksilver, by which the heat given out was absorbed. The result was 774·987 foot-pounds.

Of all his results Joule considered those given by water as the most accurate; and as he thought that even this figure should be slightly reduced, to allow for the sound produced by the motion, he finally gave 772 foot-pounds as the most probable value for the number sought.

Transforming this to French measures we obtain the result that, *To produce the quantity of heat required to raise* 1 *kilogramme of water through* 1 *degree Centigrade, work must be consumed to the amount of* 423·55 *kilogrammetres.* This appears to be the most trustworthy value among those hitherto determined, and accordingly we shall henceforward use it as the mechanical equivalent of heat, and write

$$E = 423{\cdot}55 \qquad\qquad (1).$$

In most of our calculations it will be sufficiently accurate to use the even number 424.

§ 5. *The Mechanical Unit of Heat.*

Having established the principle of the equivalence of Heat and Work, in consequence of which these two may be opposed to each other in the same expression, we are often in the position of having to sum up quantities, in which heat and work enter as terms to be added together. As, however, heat and work are measured in different ways, we cannot in such a case say simply that the quantity is the sum of the work and the heat, but either that it is *the sum of the heat and of the heat-equivalent of the work*, or *the sum of the work and of the work-equivalent of the heat.* On account of this inconvenience Rankine proposed to employ a different unit for heat, viz. that amount of heat which is equivalent to an unit of work. This unit may be called simply the Mechanical Unit of Heat. There is an obstacle to its general introduction in the circumstance that the unit of heat hitherto used is a quantity which is closely connected with the ordinary calorimetric methods (which mainly depend on the heating of water), so that the reductions required are slight, and rest on measurements of the most reliable character; while the mechanical unit, besides needing the same reductions, also requires the mechanical equivalent of heat to be known, a requirement as yet only approximately fulfilled. At the same time, in the theoretical development of the Mechanical Theory of Heat, in which the relation between heat and work often occurs, the method of expressing heat in mechanical units effects such important simplifications, that the author has felt himself bound to drop his former objections to this method, on the occasion of the present more connected exposition of that theory. Thus in what follows, unless the contrary is expressly stated, it will be always understood that heat is expressed in mechanical units.

On this system of measurement the above mentioned first main Principle of the Mechanical Theory of Heat takes a yet more precise form, since we may say that heat and its corresponding work are not merely *proportional*, but *equal* to each other.

If later on it is desired to convert a quantity of heat expressed in mechanical units back again to ordinary heat units, all that will be necessary is to divide the number given in mechanical units by E, the mechanical equivalent of heat.

§ 6. *Development of the first main Principle.*

Let any body whatever be given, and let its condition as to temperature, volume, &c. be assumed to be known. If an indefinitely small quantity of heat dQ is imparted to this body, the question arises what becomes of it, and what effect it produces. It may in part serve to increase the amount of heat actually existing in the body; in part also, if in consequence of the imparting of this heat the body changes its condition, and that change includes the overcoming of some force, it may be absorbed in the work done thereby. If we denote the total heat existing in the body, or more briefly the Quantity of Heat of the body, by H, and the indefinitely small increment of this quantity by dH, and if we put dL for the indefinitely small quantity of work done, then we can write:

$$dQ = dH + dL \text{ ....(I).}$$

The forces against which the work is done may be divided into two classes: (1) those which the molecules of the body exert among themselves, and which are therefore dependent on the nature of the body itself, and (2) those which arise from external influences, to which the body is subjected. According to these two classes of forces, which have to be overcome, the work done is divided into internal and external work. If we denote these two quantities by dJ and dW, we may put

$$dL = dJ + dW \text{.....................(2),}$$

and then the foregoing equation becomes

$$dQ = dH + dJ + dW \text{ ....(II).}$$

§ 7. *Different conditions of the Quantities J, W, and H.*

The internal and external work obey widely different laws. As regards the internal work it is easy to see that if a body, starting from any initial condition whatever, goes through a cycle of changes, and finally returns to its original condition again, then the internal work done in the whole process must cancel itself exactly. For if any definite amount, positive or negative, of internal work remained over at the end, there must have been produced thereby either an equivalent quantity of external work or a change in the body's quantity of heat; and as the same process might be repeated any number of times it would in the positive case be possible to create work or heat out of nothing, and in the negative case to get rid of work or heat without obtaining any equivalent for it; both of which results will be at once admitted to be impossible. If then at every return of the body to its original condition the internal work done becomes zero, it follows further that in any alteration whatever of the body's condition the internal work done can be determined from its initial and final conditions, without needing to know the way in which it has passed from one to the other. For if we suppose the body to be brought successively from the first condition to the second in several different ways, but always to be brought back to its first condition in exactly the same way, then the various quantities of internal work done in different ways in the first set of changes must all be equivalent to one and the same quantity of internal work done in the second or return set of changes, which cannot be true unless they are all equal to each other.

We must therefore assume that the internal forces have an Ergal, which is a quantity fully determined by the existing condition of the body at any time, without its being requisite for us to know how it arrived at that condition. Thus the internal work done is ascertained by the increment of the Ergal, which we will call J; and for an indefinitely small change of the body the differential dJ of the Ergal forms the expression for the internal work, which agrees with the notation employed in equations 2 and II.

If we now turn to the external work, we find the state of things wholly different. Even when the initial and final conditions of the body are given, the external work can take very different forms. To show this by an example, let us choose for our body a Gas, whose condition is determined by its temperature t and volume v, and let us denote the initial values of these by t_1, v_1, and the final values by t_2, v_2; let us also assume that $t_2 > t_1$, and $v_2 > v_1$. Now if the change is carried out in the following way, viz. that the gas is first expanded, at the temperature t_1, from v_1 to v_2, and then is heated, at the volume v_2, from t_1 to t_2, then the external work will consist in overcoming the external pressure which corresponds to the temperature t_1. On the other hand, if the change is carried out in the following way, viz. that the gas is first heated, at the volume v_1, from t_1 to t_2, and is then expanded, at the temperature t_2, from v_1 to v_2, then the external work will consist in overcoming the external pressure which corresponds to the temperature t_2. Since the latter pressure is greater than the former, the external work is greater in the second case than in the first. Lastly, if we suppose expansion and heating to succeed each other in stages of any kind, or to take place together according to any law, we continually obtain fresh pressures, and therewith an endless variety in the quantities of work done with the same initial and final conditions.

Another simple example is as follows. Let us take a given quantity of a liquid at temperature t, and transform it into saturated vapour of the higher temperature t_2. This change can be carried out either by heating the liquid, as a liquid, to t_2, and then vaporizing it; or by vaporizing it at t, and then heating the vapour to t_2, compressing it at the same time sufficiently to keep it saturated at temperature t_2; or finally by allowing the vaporization to take place at any intermediate temperature. The external work, which again shows itself in overcoming the external pressure during the alteration of volume, has different values in all these different cases.

The difference in the mode of alteration which, by way of example, has been thus described for two special classes of bodies, may be generally expressed by saying that the body can pass *by different paths* from one condition to the other.

Another difference, besides this, may come into play. If a body in changing its condition overcomes an external resistance, the latter may either be so great that the full force of the body is required to overcome it, or it may be less than this amount. Let us again take as example a given quantity of a gas, which at a given temperature and volume possesses a certain expansive force. If this gas expands, the external resistance which it has to overcome in so doing must clearly be smaller than the expansive force, or it would not overcome it; but the difference between them may be as small as we please, and as a limiting case we may assume them to be equal. These may also however be cases in which this difference is a finite quantity more or less considerable. If *e.g.* the vessel, in which the gas is at first confined with a given force of expansion, is suddenly put in communication with some space in which a smaller pressure exists, or with a vessel which is entirely empty, then the gas in its expansion overcomes a less external resistance than it has the power of overcoming, or in the second case no external resistance at all; and it performs in so doing a smaller amount of external work than it might perform, or in the second case no external work whatsoever.

In the original case, where pressure and reaction are at each instant equal, the gas may be compressed back again by exactly the same force which it has overcome in expanding. If however the resistance overcome is less than the force of expansion, the gas cannot be compressed back again by the same amount of force. The distinction may be expressed by saying that the expansion is *reversible* in the first case, and *not reversible* in the second.

This mode of expression may be employed in other cases, where changes of condition take place in the overcoming of any kind of resistance, and the distinction just mentioned in relation to the external work may be generally described as follows: *with a given change of condition the external work may differ in amount, according as the change takes place in a reversible or a non-reversible manner.*

§ 8. *Energy of the Body.*

In addition to the two differentials dJ and dW, which depend on the work done, we have on the right-hand side of equation (II) a third, which is the differential of H, the total heat actually existing in the body, or its quantity of Heat. This quantity H has clearly the property, also mentioned as belonging to J, that it is known as soon as the condition of the body is given, without needing to know the way in which the body has arrived at that condition.

Since the heat existing in the body and the internal work are on the same footing as regards the above most important property, and since further, on account of our ignorance as to the internal work, we generally do not know the several amounts of these two quantities but only their sum, the author, in his first Paper on Heat, published in 1850, combined the two under one designation. Following the same system, we will put

$$U = H + J \quad\text{.............................}(3),$$

which changes equation (II) into

$$dQ = dU + DW \quad\text{......................}(\text{III}).$$

The function U, first introduced by the author in the abovementioned paper, has been since adopted by other writers on Heat, and as the definition given by him—that starting from any given initial condition it expresses the sum of the increment of the heat actually existing and of the heat consumed in internal work—is somewhat long, various attempts have been made at a shorter designation. Thomson, in his paper of 1851*, called it *the mechanical energy of a body in a given state:* Kirchoff has given it the name 'Function of Activity' (Wirkungsfunction)†: lastly Zeuner, in his 'Grundzuge des mechanischen Wärmetheorie,' published 1860, has called the quantity U, when multiplied by the heat-equivalent of work, the 'Interior Heat' of the body.

This last name (as remarked in the author's former work of 1864) does not seem quite to correspond with the meaning of U; since only one part of this quantity stands for heat actually existing in the body, i.e. for *vis viva* of its molecular motion, while the other part consists of heat which has been consumed in doing internal work, and therefore exists as heat no longer. In his second edition, published 1866, Zeuner has made the alteration of calling U the *Internal Work* of the body. The author however is unable to accept this name any more than the other, inasmuch as it appears to be just as objectionably limited on the other side. Of the other two names, that of Energy, employed by Thomson, appears very appropriate, since the quantity under consideration corresponds exactly with that which is denoted by the same word in Mechanics. In what follows the quantity U will therefore be called the *Energy* of the body.

There still remains one special remark to be made with reference to the complete determination of the Ergal, and of the Energy which comprises the Ergal. Since the Ergal expresses the work which the internal forces must have performed, while the body was passing from any initial condition, taken as the starting point, to its condition at the moment under consideration, we can only determine completely the value of the Ergal for the present condition of the body, when we have previously ascertained once for all its initial condition. If this has not been done, we must conceive the function which expresses the Ergal as still containing an indeterminate constant, which depends on the initial condition. It will be obvious that it is not always necessary actually to write down this constant, but that we may conceive it as included in the function, so long as this latter is designated by a general symbol. Similarly we must conceive another such indeterminate constant as included in the other symbol which expresses the Energy of the body.

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* *Trans. Royal Soc. of Edinburgh*, Vol. xx., p. 475.

† Pogg. *Ann.* Vol. ciii., p. 177.

§ 9. *Equations for Finite changes of condition—Cyclical processes.*

If we conceive the equation (III), which relates to an indefinitely small change of condition, to be integrated for any given finite change, or for a series of successive finite changes, the integral of one term can be determined at once. For the energy U, as mentioned above, depends only on the condition of the body at the moment, and not on the way in which it has arrived at that condition. If then we put U_1 and U_2 for the initial and final values of U, we may write

$$\int dU = U_2 - U_1.$$

Hence the equation obtained by integrating (III) may be written:

$$\int dQ = U_2 - U_1 + \int dW \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4);$$

or if we denote by Q and W the two integrals $\int dQ$ and $\int dW$ which occur in this equation, and which represent respectively the total heat imparted to the body during the change, or series of changes, and the external work done, then the equation will be

$$Q = U_2 - U_1 + W \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4a).$$

As a special case, we may assume that the body undergoes a series of changes such that it is finally brought round to its initial condition. To such a series the author gave the name of *cyclical process.* As in this case the initial and final conditions of the body are the same, U_1 becomes equal to U_2, and their difference to zero. Hence for a cyclical process equations (4) and (4a) become:

$$\int dQ = \int dW \qquad (5),$$

$$Q = W \qquad (5a).$$

Thus in a cyclical process the total heat imparted to the body (i.e. the algebraical sum of all the several quantities of heat imparted in the course of the cycle, which quantities may be partly positive, partly negative) is simply equal to the total amount of external work performed.

§ 10. *Total Heat—Latent and Specific Heat.*

In former times, when heat was considered to be a substance, and when it was assumed that this substance might exist in two different forms, which were distinguished by the terms *free* and *latent*, a conception was introduced which was often made use of in calculations, and which was called the *total heat* of the body. By this was understood that quantity of heat which a body must have taken up in order to pass from a given initial condition into its present condition, and which is now contained in it, partly as free, partly as latent heat. It was supposed that this quantity of heat, if the initial condition of the body was known, could be completely determined from its present condition, without taking into account the way in which that condition had been reached.

Since, however, we have obtained in equation (4a) an expression for the quantity of heat received by the body in passing from its initial to its final condition, which expression contains the external work W, we must conclude that this quantity of heat, like the external work, depends not only on the initial and final conditions, but also on the way in which the body has passed from the one to the other. The conception of the total heat as a quantity depending only on the present condition of the body is therefore, under the new theory, no longer allowable.

The disappearance of heat during certain special changes of condition, e.g. fusion and vaporization, was formerly explained, as indicated above, by supposing this heat to pass into a special form, in which it was no longer sensible to our touch or to the thermometer, and in which it was therefore called Latent Heat. This mode of explanation has also been opposed by the author, who has laid down the principle that all heat existing in a body is appreciable by the touch and by the thermometer; that the heat which disappears under the above changes of condition exists no longer as heat, but has been converted into work; and that the heat which makes its appearance under the opposite changes (e.g. solidification and condensation) does not come from any concealed source, but is newly produced by work done on the body. Accordingly he has proposed the term Work-heat as a substitute for Latent heat in general cases.

This work, into which the heat is converted, and which in the opposite class of changes produces heat, may be of two kinds, internal or external. If e.g. a liquid is vaporized, the cohesion of its molecules must be overcome, and, since the vapour occupies a larger space than the liquid, the external pressure must be overcome also. In accordance with these two divisions of the work we also may divide the total work-heat, and call the divisions the internal and external work-heat respectively.

That quantity of heat which must be imparted to a body in order to heat it simply, without making any change in its density, was formerly known under the general name of *free* heat, or more properly, of heat *actually existing* in the body; a great part of this, however, falls into the same category as that which was formerly called *latent* heat, and for which the term *work-heat* has been proposed. For the heating of a body involves as a general rule a change in the arrangement of its molecules, which change produces in general an externally perceptible alteration of volume, but still may take place apart from such alteration. This change of arrangement requires a certain amount of work, which may be partly internal, partly external; and in doing this, work-heat is again consumed. The heat applied to the body thus serves in part only to increase the heat actually existing, the other part serving as work-heat.

On these principles the author attempted to explain (by way of example) the unusually great specific heat of water, which is much beyond that either of ice or of steam*: the assumption being that of the quantity of heat, which each receives from without in the process of heating, a larger portion is consumed in the case of water in diminishing the cohesion of the particles, and thus serves as work-heat.

From the foregoing it is seen to be necessary that, in addition to the various specific heats, which shew how much heat must be imparted to one unit-weight of a body in order to warm it through one degree under different circumstances (e.g. the specific heat of a solid or liquid body under ordinary atmospheric pressure, and the specific heat of a gas at constant volume or at constant pressure), we must also take into consideration another quantity which shews *by how much the heat actually existing in one unit-weight of a substance* (i.e. *the vis viva of the motion of its ultimate particles*) *is increased when the substance is heated through one degree of temperature.* This quantity we will name the body's *true heat-capacity.*

It would be advantageous to confine this term 'heat-capacity' (even if the word 'true' be not prefixed) strictly to the heat actually existing in the body; whereas for the total heat which must be imparted for the purpose of heating it under any given circumstances, and of which work-heat forms a part, the expression 'specific heat' might be always employed. As however the term 'heat-capacity' has hitherto been usually taken to have the same signification as 'specific heat' it is still necessary, in order to affix to it the above simplified meaning, to add the epithet 'true.'

§ 11. *Expression for the External Work in a particular case.*

In equation (III) the external work is denoted generally by dW. No special assumption is thereby made as to the nature of the external forces which act on the body, and on which the external work depends. It is, however, worth while to consider one special case which occurs frequently in practice, and which leads to a very simple determination of the external work, viz. the case where the only external force acting on the body, or at least the only force which needs to be referred to in the determination of the work, is a pressure acting on the exterior surface of the body; and in which this pressure (as is always the case with liquid and gaseous bodies, provided no other forces are acting, and which may be the case even with solid bodies) is the same at all points of the surface, and everywhere normal to it. In this case there is no need, in order to determine the external work, that we should consider the body's alterations in form and its expansion in particular directions, but only its total alteration in volume.

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* Pogg. *Ann.* Vol. LXXIX., p. 375, and *Collection of Memoirs*, Vol. I., p. 23.

As an illustrative case, let us take a cylinder, as shewn in Fig. 1, closed by an easily moving piston P, and containing some expansible substance, e.g. a gas, under a pressure per unit-area represented by p. The section of the cylinder, or the area of the piston, we may call a. Then the total pressure which acts on the piston, and which must be overcome in raising it, is pa. Now if the piston stands originally at a height h above the bottom of the cylinder, and is then lifted through an indefinitely small distance dh, the external work performed in the lifting will be expressed by the equation

$$dW = pa\,dh.$$

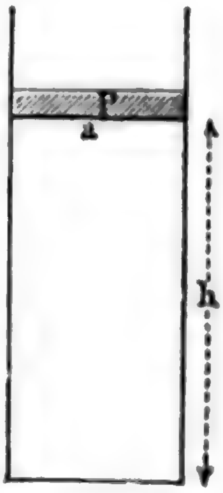

Fig. 1.

But if v be the volume of the gas we have $v = ah$, and therefore $dv = adh$; whence the above equation becomes

$$dW = pdv \text{ .... } (6).$$

This same simple form is assumed by the differential of the external work for any form of the body, and any kind of expansion whatever, as may be easily shewn as follows. Let the full line in Fig. 2 represent the surface of the body in its original condition, and the dotted line its surface after an indefi-

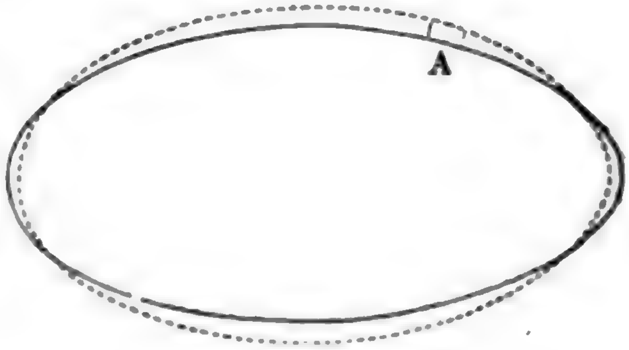

Fig. 2.

nitely small change of form and volume. Let us consider any element $d\omega$ of the original surface at the point A. Let a normal drawn to this element of surface cut the second surface at a distance du from the first, where du is taken as positive if the position of the second surface is outside the space contained within the original surface, and negative if it is inside. Now let us suppose an indefinite number of such normals to be drawn through every point in the perimeter of the surface-element $d\omega$ to the second surface; there will then be marked out an indefinitely small prismatic space, which has $d\omega$ as its base, and du as its height, and whose volume is therefore expressed by $d\omega du$. This indefinitely small volume forms the part of the increase of volume of the body corresponding to the element of surface $d\omega$. If then we integrate the expression $d\omega du$ all over the surface of the body, we shall obtain the whole increase in volume, dv, of the body, and if we agree to express integration over the surface by an integral sign with suffix ω, we may write

$$dv = \int_\omega du\,d\omega \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \;(7).$$

Now if, as before, we denote the pressure per unit of surface by p, the pressure on the element $d\omega$ will be $pd\omega$. Therefore the part of the external work, which corresponds to the element $d\omega$, and is described by saying that the element under the action of the external force $pd\omega$ is pushed outwards at right angles through the distance du, will be expressed by the product $pd\omega du$. Integrating this over the whole surface, we obtain for the total external work,

$$dW = \int_\omega p\,du\,d\omega.$$

As p is equal over the whole surface, the equation may be written:

$$dW = p\int_\omega du\,d\omega,$$

or, by equation (7),

$$dW = pdv,$$

which is the same as equation (6) given above.

Adopting this equation, we may give to equation (III), for the case in which the only external force is a uniform pressure normal to the surface, the following form:

$$dQ = dU + pdv \qquad \text{(IV)}.$$

This last equation, which forms the mathematical expression most in use for the first main principle of the Mechanical Theory of Heat, we will in the next place apply to a class of bodies, which are distinguished for the simplicity of their laws, and for which the equation takes accordingly a peculiarly simple form, so that the required calculations can be easily performed.

CHAPTER II.

ON PERFECT GASES.

§ 1. *The Gaseous condition of bodies.*

Among the laws which characterize bodies in the gaseous condition the foremost place must be given to those of Mariotte and Gay Lussac, which may be expressed together in a single equation as follows. Given a unit-weight of a gas, which at freezing temperature, and under any standard pressure p_0 (*e.g.* that of the atmosphere) has the volume v_0; then if p and v be its pressure and volume at any temperature t (in Centigrade measure) the following equation will hold:

$$pv = p_0 v_0 (1 + \alpha t) \text{.....................} (1),$$

wherein the quantity α, which is usually termed the coefficient of expansion, although it really relates to the change of pressure as well as the change of volume, has one and the same value for every kind of gas.

Regnault has indeed recently proved by careful experiment that these laws are not strictly accurate; but the deviations are for permanent gases very small, and become of importance only for gases which are capable of condensation. It seems to follow that the laws are the more nearly exact, the further a gas is removed, as to pressure and temperature, from its point of condensation. Since for permanent gases under ordinary conditions the exactness of the law is already so great, that for most purposes of research it may be taken as perfect, we may imagine for every gas an ultimate condition, in which the exactness is really perfect; and in what follows we will assume this ideal condition to be actually reached, calling for brevity's sake all gases, in which this is assumed to hold, Perfect Gases.

As however the quantity α, according to Regnault's determinations, is not absolutely the same for all the gases which have been examined, and has also somewhat different values for one and the same gas under different conditions, the question arises, what value we are to assign to α in the case of perfect gases, in which such differences can no longer appear. Here we must refer to the values of α which have been found to be correct for various permanent gases. By experiments made on the system of increasing the pressure while keeping the volume constant, Regnault found the following numbers to be correct for various permanent gases:

Atmospheric Air	0·003665.
Hydrogen..................	0·003667.
Nitrogen	0·003668.
Carbonic Oxide	0·003667.

The differences here are so small, that it is of little importance what choice we make; but as it was with atmospheric air that Regnault made the greatest number of experiments, and as Magnus was led in his researches to a precisely similar result, it appears most fitting to select the number 0·003665.

Regnault, however, by experiments made on the other system of keeping the pressure constant and increasing the volume, has obtained a somewhat different value for α in the case of atmospheric air, viz. 0·003670. He has further observed that rarefied air gives a somewhat smaller, and compressed air a somewhat larger, coefficient of expansion than air of ordinary density. This latter circumstance has led some physicists to the conclusion that, as rarefied air is nearer to the perfect gaseous condition than air of ordinary density, we ought to assume for perfect gases a smaller value than 0·003665. Against this it may be urged, that Regnault observed no such dependence of the coefficient of expansion on the density in the case of hydrogen, but after increasing the density threefold obtained exactly the same value as before; and that he also found that hydrogen, in its deviation from the laws of Mariotte and Gay Lussac, acts altogether differently, and for the most part in exactly the opposite way, from atmospheric air. In these circumstances the author considers that additional weight is given to the result taken above from the figure for atmospheric air; since it will hardly be questioned that hydrogen is at least as near as atmospheric air to the condition of a perfect gas, and therefore in drawing conclusions relative to that condition the behaviour of the one is as much to be noted as that of the other.

It appears therefore to be the best course (so long as fresh observations have not furnished a more satisfactory starting point for wider conclusions) to adhere to the figure which, under the pressure of one atmosphere, has been found to agree almost exactly for atmospheric air and for hydrogen; and thus to write:

$$\alpha = 0{\cdot}003665 = \tfrac{1}{273} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2).$$

If we denote the reciprocal $\frac{1}{\alpha}$ by a we may also write the equation thus;

$$pv = \frac{p_0 v_0}{a}(a + t) \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3).$$

And if for brevity we put:

$$R = \frac{p_0 v_0}{a} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4),$$

$$T = a + t \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5),$$

we then obtain the equation in the form

$$pv = RT \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6).$$

R is here a constant which depends on the nature of the gas and is inversely proportional to its specific gravity*. T represents the temperature, provided this is measured not from the freezing point, but from a zero point lying a degrees lower. The temperature thus measured from $-a$ we shall term the Absolute Temperature, a name which will be more fully explained further on. Taking the value of α given in equation (2) we obtain

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* For R is proportional to the volume of a unit of weight of the gas at standard pressure and temperature; and is therefore inversely proportional to the weight of a unit of volume, i.e. to the specific gravity. (*Translator.*)

$$\left.\begin{aligned} a &= \frac{1}{\alpha} = 273 \\ T &= 273 + t \end{aligned}\right\} \qquad (7).$$

§ 2. *Approximate Principle as to Heat absorbed by Gases.*

In an experiment of Gay Lussac's, a vessel filled with air was put in communication with an exhausted receiver of equal size, so that half the air from the one passed over into the other. On measuring the temperature of each half, and comparing it with the original temperature, he found that the air which had passed over had become heated, and the air which remained behind had become cooled, to exactly the same degree; so that the mean temperature was the same after the expansion as before. He thus proved that in this kind of expansion, in which no external work was done, no loss of heat took place. Joule, and after him Regnault, carried out similar experiments with greater care, and both were led to the same result.

The principle here involved may also be deduced, without reference to special experiments, from certain properties of gases otherwise ascertained, and its accuracy may thus be checked. Gases shew so marked a regularity in their behaviour (especially in the relation between volume, pressure, and temperature, expressed by the law of Mariotte and Gay Lussac), that we are thereby led to the supposition that the mutual action between the molecules, which goes on in the interior of solid and liquid bodies, is absent in the case of gases; so that heat, which in the former cases has to overcome the internal resistances, as well as the external pressure, in order to produce expansion, in the case of gases has to do with external pressure alone. If this be so, then, if a gas expands at constant temperature, only so much heat can thereby be absorbed as is required for doing the external work. Again, we cannot suppose that the total amount of heat actually existing in the body is greater after it has expanded at constant temperature than before. On these assumptions we obtain the following principle: *a permanent gas, if it expands at a constant temperature, absorbs only* *so much heat as is required for the external work which it performs in so doing.*

We cannot of course give to this principle any greater validity than that of the principles from which it springs, but must rather suppose that for any given gas it is true to the same extent only in which the law of Mariotte and Gay Lussac is true. It is only for perfect gases that its absolute accuracy may be assumed. It is on this understanding that the author brought this principle into application, combined it as an approximate assumption with the two main principles of the Mechanical Theory of Heat, and used it for establishing more extended conclusions.

More recently Mr, now Sir William Thomson, who at first did not agree with one of the conclusions so deduced, undertook in conjunction with Joule to test experimentally the accuracy of the principle*; and for this purpose instituted with great care a series of skilfully conceived experiments, which, on account of their importance, will be more fully and exactly discussed further on. These have completely confirmed the truth not only of the general principle, but also of the remark added by the author as to its degree of exactness. In the permanent gases on which they experimented, viz. atmospheric air and hydrogen, the principle was found so nearly exact that the deviations might for the purpose of most calculations be neglected; while in the non-permanent gas selected for experiment (Carbonic Acid) somewhat greater deviations were observed, exactly as might have been expected from the behaviour of that gas in other respects.

After this we may with the less scruple apply the principle, as being exact for actually existing gases in the same degree as the law of Mariotte and Gay Lussac, and absolutely exact in the case of perfect gases.

§ 3. *On the Form which the Equation expressing the first main Principle assumes, in the case of perfect gases.*

We now return to equation (IV), viz.:

$$dQ = dU + pdv,$$

in order to apply it to the case of a perfect gas, of which we assume as before one unit of weight to be given.

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* *Phil. Trans.* 1853, 1854, 1862.

The condition of the gas is completely determined, when its temperature and volume are known; or it may be determined by its temperature and pressure, or by its volume and pressure. We will at present choose the first-named quantities, temperature and volume, to determine the condition, and accordingly treat T and v as the independent variables, on which all other quantities relating to the condition of the gas depend. If then we regard the energy U of the gas as being also a function of these two variables, we may write

$$dU = \frac{dU}{dT} dT + \frac{dU}{dv} dv,$$

whence equation (IV) becomes

$$dQ = \frac{dU}{dT} dT + \left(\frac{dU}{dv} + p\right) dv \text{.............} (8).$$

This equation, which in the above form holds not only for a gas, but for any body whose condition is determined by its temperature and volume, may be considerably simplified for gaseous bodies, on account of their peculiar properties.

The quantity of heat, which a gas must absorb in expanding at constant temperature through a volume dv, is generally denoted by $\frac{dQ}{dv} dv$. As by the approximate assumption of the last Section this heat is equal to the work done in the expansion, which is expressed by pdv, we have the equation:

$$\frac{dQ}{dv} dv = pdv, \quad \text{or} \quad \frac{dQ}{dv} = p.$$

But from equation (8)

$$\frac{dQ}{dv} = \frac{dU}{dv} + p:$$

hence from the last two equations we obtain

$$\frac{dU}{dv} = 0 \text{..........................} (9).$$

Hence we conclude that in a perfect gas the energy U is independent of the volume, and can only be a function of the temperature.

If in equation (8) we put $\frac{dU}{dv}=0$, and substitute for $\frac{dU}{dT}$ the symbol C_v, it becomes

$$dQ = C_v dT + pdv \quad\ldots\ldots\ldots\ldots(10).$$

From the form of this equation we see that C_v denotes the *Specific Heat of the Gas at constant volume*, since $C_v dT$ expresses the quantity of heat which must be imparted to the gas in order to heat it from T to $T+dT$, when dv is equal to zero. As this Specific Heat $=\frac{dU}{dT}$, i.e. is the differential coefficient with respect to temperature of a function of the temperature only, it can itself also be only a function of temperature.

In equation (10) all the three quantities T, v, and p are found; but since by equation (6) $pv=Rt$, it is easy to eliminate one of them; and by eliminating each in succession we obtain three different forms of the equation.

Eliminating p we obtain,

$$dQ = C_v dT + \frac{RT}{v} dv \quad\ldots\ldots\ldots\ldots(11).$$

Again, to eliminate v we put $v=\frac{RT}{p}$; whence we have

$$dv = \frac{R}{p} dT - \frac{RT}{p^2} dp.$$

If we substitute this value of dv in equation (10), and then combine the two terms of the equation which contain dT, we obtain

$$dQ = (C_v + R)\, dT - \frac{RT}{p} dp \quad\ldots\ldots\ldots\ldots(12).$$

Lastly, to eliminate T, we obtain from equation (6), by differentiation,

$$dT = \frac{vdp + pdv}{R}.$$

Substituting in equation (10)

$$dQ = \frac{C_v}{R} vdp + \frac{C_v + R}{R} pdv \text{.............} (13).$$

§ 4. *Deductions as to the two Specific Heats, and transformation of the foregoing equations.*

In the same way as we see from equation (10) that the quantity C_v, which appears as factor of dT, denotes the specific heat at constant temperature, we may see from equation (12) that the factor of dT in that equation, viz. $C_v + R$, expresses the *Specific Heat at constant pressure.* If therefore we denote this Specific Heat by C_p we may put

$$C_p = C_v + R \text{......................} (14),$$

which equation gives the relation between the two Specific Heats.

Since R is a constant, and C_v, as shewn above, is a function of temperature only, it follows from equation (14) that C_p also can only be a function of temperature.

When the author first drew in this manner from the Mechanical Theory of Heat the conclusion that the two Specific Heats of a permanent gas must be independent of its density, or in other words of the pressure to which it is subjected, and could depend only on its temperature; and when he added the further remark that they were thus in all probability constant; he found himself in opposition to the then prevailing views on the subject. At that time it was considered to be established from the experiments of Suermann, and from those of de la Roche and Bérard, that the specific heat of a gas depended on the pressure; and the circumstance that the new theory led to an opposite conclusion produced mistrust of the theory itself, and was used by A. von Holtzmann as a weapon of attack against it.

Some years later, however, followed the first publication of the splendid experiments of Regnault on the specific heat of gases*, in which the influence of pressure and temperature on the specific heat was made a subject of special investigation. Regnault tested atmospheric air at pressures from 1 to 12 atmospheres, and hydrogen at from 1 to 9 atmospheres, but could detect no difference in their specific heats. He tested them also at different temperatures, viz. between -30° and $+10^\circ$, between 0° and 100°, and between 0° and 200°; and here also he found the specific heat always the same*. The result of his experiments may thus be expressed by saying that, within the limits of pressure and temperature to which his observations extended, the specific heat of permanent gases was found to be constant.

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* *Comptes Rendus*, Vol. xxxvi., 1853; also *Relation des expériences*, Vol. ii.

It is true that these direct explanatory researches were confined to the specific heat at constant pressure; but there will be little scruple raised as to assuming the same to be correct for the other specific heat, which by equation (14) differs from the former only by the constant *R*. Accordingly in what follows we shall treat the two specific heats, at least for perfect gases, as being constant quantities.

By help of equation (14) we may transform the three equations (11), (12) and (13), which express the first main principle of the Mechanical Theory of Heat as applied to gases, in such a way that they may contain, instead of the Specific Heat at constant volume, the Specific Heat at constant density; which may perhaps appear more suitable, since the latter, as being determined by direct observation, ought to be used more frequently than the former. The resulting equations are:

$$\left.\begin{aligned} dQ &= (C_p - R)\,dT + \frac{RT}{v}\,dv \\ dQ &= C_p\,dT - \frac{RT}{p}\,dp \\ dQ &= \frac{C_p - R}{R}\,vdp + \frac{C_p}{R}\,pdv \end{aligned}\right\}\ldots\ldots\ldots\ldots\ldots(15).$$

Lastly, we may introduce both Specific Heats into the equations, and eliminate *R*, by which means the resulting

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* The numbers obtained for atmospheric air (*Rel. des Exp.* Vol. II., p. 108) are as follows in ordinary heat units:

between	-30°	and	$+10^\circ$	0·23771,
,,	0°	,,	100°	0·23741,
,,	0°	,,	200°	0·23751,

which may be taken as practically the same.

equations become symmetrical as to p and v, as follows:

$$\left.\begin{aligned} dQ &= C_v dT + (C_p - C_v)\frac{T}{v}dv \\ dQ &= C_p dT + (C_v - C_p)\frac{T}{p}dp \\ dQ &= \frac{C_v}{C_p - C_v}vdp + \frac{C_p}{C_p - C_v}pdv \end{aligned}\right\} \text{..........}(16).$$

In the above equations the specific heats are expressed in mechanical units. If we wish to express them in ordinary heat units, we have only to divide these values by the Mechanical Equivalent of Heat. Thus if we denote the specific heats, as expressed in ordinary heat units, by c_v and c_p, we may put

$$c_v = \frac{C_v}{E}, \quad c_p = \frac{C_p}{E} \text{..................} (17).$$

Applying these equations to equation (14), and dividing by E, we have

$$c_p = c_v + \frac{R}{E} \text{............................}(18).$$

§ 5. *Relation between the two Specific Heats, and its application to calculate the Mechanical Equivalent of Heat.*

If a system of Sound-waves spreads itself through any gas, e.g. atmospheric air, the gas becomes in turn condensed and rarefied; and the velocity with which the sound spreads depends, as was seen by Newton, on the nature of the changes of pressure produced by these changes of density. For very small changes of density and pressure the relation between the two is expressed by the differential coefficient of the pressure with respect to the density, or (if the density, i.e. the weight of a unit of volume, is denoted by ρ) by the differential coefficient $\frac{dp}{d\rho}$. Applying this principle we obtain for the velocity of sound, which we will call u, the following equation

$$u = \sqrt{g\frac{dp}{d\rho}} \text{........................}(19),$$

in which g represents the accelerating force of gravity.

Now in order to determine the value of the differential coefficient $\frac{dp}{d\rho}$ Newton used the law of Mariotte*, according to which pressure and density are proportional to each other. He therefore put $\frac{p}{\rho}=$ constant, whence by differentiation:

$$\frac{\rho dp - pd\rho}{\rho^2}=0,$$

and therefore

$$\frac{dp}{d\rho}=\frac{p}{\rho}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(20);$$

whence (19) becomes

$$u=\sqrt{g\frac{p}{\rho}}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(21).$$

The velocity calculated by this formula did not however agree with experiment, and the reason of this divergence, after it had been long sought for in vain, was at last discovered by Laplace.

The law of Mariotte in fact holds only if the change of density takes place at constant temperature. But in sound vibrations this is not the case, since in every condensation a heating of the air takes place, and in every rarefaction a cooling. Accordingly at each condensation the pressure is increased, and at each rarefaction diminished, to a greater extent than accords with Mariotte's law. The question now arises how, under these circumstances, can the value of $\frac{dp}{d\rho}$ be determined.

Since the condensations and rarefactions follow each other with great rapidity, the exchange of heat that can take place during each short period between the condensed and rarefied parts of the gas must be very small. Neglecting this, we have to do with a change of density, in which the quantity of gas under consideration receives no heat and gives forth none; and we may thus, in applying to this case the differential equations of the last section, put $dQ = 0$. Hence, e.g. from the last of equations (16), we obtain:

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* This law is commonly known in England as 'Boyle's law,' as being originally due to Boyle. (*Translator.*)

$$\frac{C_v}{C_p - C_v} v dp + \frac{C_p}{C_p - C_v} p dv = 0,$$

or

$$C_v v dp + C_p p dv = 0.$$

Now, since the volume v of one unit of weight is the reciprocal of the density, we may put $v = \frac{1}{\rho}$, and therefore $dv = \frac{-d\rho}{\rho^2}$; whence the equation becomes

$$C_v \frac{dp}{\rho} - C_p \frac{p d\rho}{\rho^2} = 0,$$

or

$$\frac{dp}{d\rho} = \frac{C_p}{C_v} \frac{p}{\rho} \text{ ....(22).}$$

This value of the Differential Coefficient $\frac{dp}{d\rho}$ differs from that deduced from Mariotte's law, and given in (20), by containing as factor the ratio of the two Specific Heats. If for simplicity we put

$$k = \frac{C_p}{C_v} \text{ ....(23),}$$

the last equation becomes

$$\frac{dp}{d\rho} = k \frac{p}{\rho} \text{ ....(24).}$$

Substituting this value of $\frac{dp}{d\rho}$ in equation (19), we get instead of (21)

$$u = \sqrt{kg \frac{p}{\rho}} \text{ ....(25).}$$

From this equation the velocity of sound u can be calculated if k is known; or, on the other hand, if the velocity of sound is known by experiment, we can apply the equation to calculate k, changing it first into the form

$$k = \frac{u^2 \rho}{gp} \text{ ....(26).}$$

The velocity of sound in air has been several times determined with great care by various physicists, whose results agree with each other very closely. According to the experiments of Bravais and Martens* the velocity at freezing temperature is 332·4 m. per second (1090·6 feet). We will insert this value in equation (26). We may also give g its recognized value 9·809 m. (32·2 feet). To determine the quotient $\frac{\rho}{p}$ we may give the pressure p any value we please, but we must then assign to the density ρ the value corresponding to that pressure. We will assume p to be the pressure of 1 atmosphere. This must be expressed in the formula by the amount of weight supported per unit of surface. As this weight is equal to that of a column of quicksilver, whose base is 1 sq. m. and height 760 mm., and which therefore has a volume of 760 cubic decimetres, and as, according to Regnault, the Specific Weight of quicksilver at 0°, as compared with water at 4°, is 13·596, we obtain

$$p = 1 \text{ atmosphere} = 760 \times 13{\cdot}596 = 10333 \text{ kg. per sq. metre.}$$

Lastly, ρ is the weight of a cubic metre of air under the assumed pressure of 1 atmosphere and at temperature 0°, which, according to Regnault, is 1·2932 kg. Substituting these values in equation (26) we obtain

$$k = \frac{(332{\cdot}4)^2 \times 1{\cdot}2932}{9{\cdot}809 \times 10333} = 1{\cdot}410.$$

Having thus determined the quantity k for atmospheric air, we can now use equation (18) to calculate the quantity E, i.e. the Mechanical Equivalent of Heat, as was first done by Mayer. For we have from (18)

$$E = \frac{R}{c_p - c_v};$$

and, if we again denote by k the quotient $\frac{c_p}{c_v}$, which is the same as $\frac{C_p}{C_v}$, and accordingly substitute $\frac{c_p}{k}$ for c_v, we have

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* *Ann. de Chim.* III., 13, 5; and *Pogg. Ann.* Vol. LXVI., p. 351.

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$$E = \frac{kR}{(k-1)\,c_p} \text{ ....(27).}$$

Here we may substitute for k its value 1·410 just found, and for c_p its value as given by Regnault, 0·2375. It then remains to determine R, or $\frac{p_0 v_0}{a}$. To do this, let us again take p_0 as the pressure of 1 atmosphere, which, as seen above, is equal to 10333, and we then have for v_0 the volume in cubic metres of 1 kg. of air under the above pressure of 1 atmosphere and at temperature 0°, which according to Regnault is 0·7733. Lastly we have already assumed the value of a to be 273. The value of R for atmospheric air will therefore be given by the equation

$$R = \frac{10333 \times 0{\cdot}7733}{273} = 29{\cdot}27.$$

Substituting these values for k, c_p, and R in equation (27) we obtain

$$E = \frac{1{\cdot}410 \times 29{\cdot}27}{0{\cdot}410 \times 0{\cdot}2375} = 423{\cdot}8.$$

This figure agrees very closely with that determined by Joule from the friction of water, viz. 423·55. In fact it must be admitted that the agreement is more close than, considering the degree of uncertainty as to the data used in the calculation, we could have had any right to expect; so that chance must have assisted in some degree to produce it. In any case, however, the agreement forms a striking confirmation of the equations deduced for permanent gases.

§ 6. *Various Formulæ relating to the Specific Heats of Gases.*

If in equation (18), p. 48, we consider the quantity E as known, we may apply that equation to calculate the specific heat at constant volume from that at constant pressure, which is known from experiment. This application is of special importance, because the method of deducing the ratio of the two specific heats from the velocity of sound is only practicable in the case of the very few gases for which that velocity has been experimentally determined. For all others, equation (18) offers the only means as yet discovered of calculating the specific heat at constant volume from that at constant pressure.

It must here be observed that equation (18) is exactly true only for perfect gases, although it gives at least approximate results for other gases. The circumstance has also to be considered, that the determination of the specific heat of a gas at constant pressure is the more difficult, and therefore the value determined the less reliable, in proportion as the gas is less permanent in its character, and thus diverges more widely in its behaviour from the laws of a perfect gas; therefore, as there is no need to seek in our calculations a greater accuracy than the experimental values themselves can possibly possess, we may treat the mode of calculation employed as sufficiently complete for our purpose.

Accordingly we begin by putting equation (18) in the form

$$c_v = c_p - \frac{R}{E} \text{ ....} \quad (28).$$

Here for E we shall use the value 423·55. R is determined by equation (4)

$$R = \frac{p_0 v_0}{a},$$

where $p_0 v_0$ are the pressure and volume at the temperature of freezing. Should it be difficult to make observations on the gas at this temperature (as is the case with many vapours) we may also, by equation (6), give R the value

$$R = \frac{pv}{T} \text{ ....} \quad (29),$$

where p, v, and T are any three corresponding values of pressure, volume, and absolute temperature.

This quantity R, as already observed, is only so far dependent on the nature of the gas, that it is inversely proportional to its specific gravity. For if we denote by v' the volume of a unit of weight of air at temperature T and pressure p, and by R' the corresponding value of R, we have

$$R' = \frac{pv'}{T}.$$

Combining this with equation (29),

$$R = R' \frac{v}{v'}.$$

But $\frac{v}{v'}$ is the ratio of the volumes of equal weights of the two gases, and is therefore the reciprocal of the ratio of the weights of equal volumes, which ratio is called the Specific Gravity of the gas, as compared with common air. If we call this specific gravity d, the last equation becomes

$$R = \frac{R'}{d} \qquad \text{.......................... (30).}$$

Substituting this value of R in (28) we obtain

$$c_v = c_p - \frac{R'}{Ed} \qquad \text{......................(31).}$$

The quantity here denoted by R', i.e. the value of R for atmospheric air, has been already determined in § 5 to be equal to 29·27. Hence further,

$$\frac{R'}{E} = \frac{29{\cdot}27}{423{\cdot}55} = 0{\cdot}0691,$$

whence the equation, which serves to determine the Specific Heat at constant volume, takes this simple form:

$$c_v = c_p - \frac{0{\cdot}0691}{d} \qquad \text{.................... (32).}$$

If in the next place we apply this equation to the case of air, for which $d = 1$, and for the sake of distinction denote by accented letters the two specific heats for air, we get the following equation:

$$c'_v = c'_p - 0{\cdot}0691 \qquad \text{.................. (33),}$$

and substituting for c'_p its value according to Regnault, which is 0·2375, we obtain the result

$$c'_v = 0{\cdot}2375 - 0{\cdot}0691 = 0{\cdot}1684 \ldots\ldots\ldots (34)^*.$$

For the other gases the equation may be given in the following form:

$$c_v = \frac{c_p d - 0{\cdot}0691}{d} \ldots\ldots\ldots\ldots\ldots\ldots (35),$$

which, as will be seen later, is specially convenient for the application of the values given by Regnault for specific heats at constant pressure.

The specific heats denoted by c_p and c_v relate to a unit of weight of the gas, and have for unit the ordinary unit of heat, i.e. the quantity of heat required to raise a unit of weight of water from the temperature 0° to 1°. We may thus say that the gas, in relation to the heat which it requires to raise its temperature either at constant pressure or constant volume, is referred as regards weight to the standard of water.

With gases however it is desirable to refer to the standard of air as regards volume; i.e. so to determine the specific heat, as to compare the quantity of heat, which the gas requires to raise its temperature through 1°, with the quantity of heat which an equal volume of air, taken at the same temperature and pressure, requires to raise its temperature to the same extent. We may use this kind of comparison in the case of both the specific heats, inasmuch as we assume in the one case that both the gas under consideration and the atmospheric air are heated at constant pressure, and in the other that they are both heated at constant volume. The specific heats thus determined may be denoted by γ_p and γ_v.

As we denote by v the volume which a unit weight of gas assumes at a given pressure and temperature, the quantity of heat, which a unit-volume of the gas absorbs at constant pressure in being heated through 1°, will be expressed by $\frac{c_p}{v}$, or in the case of atmospheric air by $\frac{c'_p}{v'}$. The specific heat γ_p is found by dividing the former quantity by the latter, or,

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* It will be seen that c_v' and c_p' fulfil the condition found above for perfect gases; $\frac{c_p}{c_v} = 1{\cdot}410$. (*Translator.*)

$$\gamma_p = \frac{c_p}{v} \times \frac{b'}{c'_p} = \frac{c_p}{c'_p} \times \frac{v'}{v} = \frac{c_p}{c'_p} d \text{ .... } (36).$$

Similarly $$\gamma_v = \frac{c_v}{c'_v} d \text{ .... } (37).$$

In the first of these two equations we may give to c'_p its value as found by Regnault, 0·2375; the equation then becomes

$$\gamma_p = \frac{c_p d}{0{\cdot}2375} \text{ .... } (38).$$

In the second we may put for c'_v, according to (34), the value 0·1684, and for c_v the expression given in (35); whence we have

$$\gamma_v = \frac{c_p d - 0{\cdot}0691}{0{\cdot}1684} \text{ .... } (39).$$

§ 7. *Numerical Calculation of the Specific Heat at constant Volume.*

The formulæ developed in the last section have been applied by the author to calculate from the values which Regnault has determined by his researches for the Specific Heat at constant Pressure of a large number of gases and vapours, the corresponding values of the Specific Heat at constant Volume. In so doing he has in some sort recalculated one of the two series of numbers given by Regnault himself; who has expressed the Specific Heat at constant Pressure in two different ways, and has brought together the resulting numbers in two series, one of which is superscribed 'en poids,' and the other 'en volume.' The first series contains the values which result, if the gases in question are compared weight by weight with water, in relation to the quantity of heat required to warm them through 1°; in other words, the values of the quantities denoted above by c_p. The numbers in the second series are simply obtained from those in the first by multiplying them by the corresponding specific gravity, i. e. they are the values of the product $c_p d$.

These latter numbers were no doubt those most easily calculated from the observed values of c_p; but their signification is somewhat complicated. With them the quantity of heat has for its unit the ordinary unit of heat, whilst the volume to which they refer is that which a unit-weight of atmospheric air assumes, when under the same temperature and pressure as the gas under consideration. The tediousness of the verbal description thus required makes the numbers troublesome to understand and to apply; moreover this mode of expressing the Specific Heat of gases has been used, so far as the author knows, by no previous writer. In considering gases with reference to volume, it has in all other cases been customary to compare the quantity of heat, which a given gas requires to raise its temperature through 1°, with the quantity of heat which an equal volume of atmospheric air requires under the same conditions for the same purpose, or, as briefly expressed above, by *comparing the gas, volume for volume, with air*. The numbers thus obtained are remarkable for their simplicity, and allow the laws which hold as to the specific heats of the gas to be treated with special clearness.

It will therefore, the author believes, be found an advantage that he has calculated, from the values given by Regnault under the heading 'en volume' for the product $c_p d$, the values of the quantity γ_p, defined above. All that was required for this, by (38), was to divide the values of $c_p d$ by 0·2375.

He has further calculated the values of c_v and γ_v; calculations which by equations (35) and (39) could be very simply performed, by taking from the values of the product $c_p d$ the number 0·0691, and dividing the remainder by d, or by 0·1684, respectively.

The numerical values thus calculated are brought together in the annexed table, in which the different columns have the following signification:

Column I. gives the name of the gas.

Column II. gives the Chemical composition, and this expressed in such a way that the diminution of volume produced by the combination can be immediately observed. For in each case those volumes of the simple gas are given, which must combine in order to give Two Volumes of the compound gas. Thus we assume for Carbon, as a gas, such an hypothetical volume as we must assume, in order to say that one volume of Carbon unites with one volume of Oxygen to make Carbonic Oxide, or with two volumes to make Carbonic acid. Again, when, e.g. Alcohol is denoted in the Table by C_2H_6O, this means that two volumes of the hypothetical carbon gas, six volumes of Hydrogen, and one volume of Oxygen, make up together two volumes of Alcoholic vapour. For sulphur-gas the specific gravity used to determine its volume is that found by Sainte-Claire Deville and Troost for very high temperatures, viz. 2·23. In the five last combinations in the Table, which contain Silicon, Phosphorus, Arsenic, Titanium, and Tin, these simple elements are denoted by their ordinary chemical signs, without reference to their volumes in the gaseous condition, because the gaseous volumes of these elements are partly still unknown, partly hampered with certain irregularities not yet thoroughly cleared up.

Column III. gives the Density of the gas, using the values given by Regnault.

Column IV. gives the Specific Heat at constant Pressure as compared, weight for weight, with water, or in other words referred to a unit-weight of the gas and expressed in ordinary units of heat. These are the numbers given by Regnault under the heading 'en poids.'

Column V. gives the Specific Heat at constant Pressure compared, volume for volume, with air, calculated by dividing by 0·2375 the numbers given by Regnault under the heading 'en volume.'

Column VI. gives the Specific Heat at constant Volume compared, weight for weight, with water, calculated by equation (35).

Column VII. gives the Specific Heat at constant Volume compared, volume for volume, with air, calculated by equation (39).

I.	II.	III.	IV.	V.	VI.	VII.
Name of the Gas.	Chemical Composition.	Density.	Specific heat at constant Pressure		Specific heat at constant Volume	
			compared weight for weight with Water.	compared volume for volume with Air.	compared weight for weight with Water.	compared volume for volume with Air.
Atmospheric Air		1	0·2375	1	0·1684	1
Oxygen	O_2	1·1056	0·21751	1·013	0·1551	1·018
Nitrogen	N_2	0·9713	0·24380	0·997	0·1727	0·996
Hydrogen...	H_2	0·0692	3·40900	0·993	2·411	0·990
Chlorine	Cl_2	2·4502	0·12099	1·248	0·0928	1·350
Bromine	Br_2	5·4772	0·05552	1·280	0·0429	1·395
Nitric Oxide	$N O$	1·0384	0·2317	1·013	0·1652	1·018
Carbonic Oxide.........	$C O$	0·9673	0·2450	0·998	0·1736	0·997
Hydrochloric Acid.....	$H Cl$	1·2596	0·1852	0·982	0·1304	0·975
Carbonic Acid..........	$C O_2$	1·5201	0·2169	1·39	0·172	1·55
Nitric Acid.	$N_2 O$	1·5241	0·2262	1·45	0·181	1·64
Steam	$H_2 O$	0·6219	0·4805	1·26	0·370	1·36
Sulphuric Acid.........	$S O_2$	2·2113	0·1544	1·44	0·123	1·62
Hydro-sulphuric Acid.	$H_2 S$	1·1747	0·2432	1·20	0·184	1·29
Carbonic di-sulphide .	$C S_2$	2·6258	0·1569	1·74	0·131	2·04
Carburetted Hydrogen	$C H_4$	0·5527	0·5929	1·38	0·468	1·54
Chloroform	$C H Cl_3$	4·1244	0·1567	2·72	0·140	3·43
Olefiant Gas............	$C_2 H_4$	0·9672	0·4040	1·75	0·359	2·06
Ammonia	$N H_3$	0·5894	0·5084	1·26	0·391	1·37
Benzine..................	$C_6 H_6$	2·6942	0·3754	4·26	0·350	5·60
Oil of Turpentine......	$C_{10} H_{16}$	4·6978	0·5061	10·01	0·491	13·71
Wood Spirit	$C H_4 O$	1·1055	0·4580	2·13	0·395	2·60
Alcohol..................	$C_2 H_6 O$	1·5890	0·4534	3·03	0·410	3·87
Ether......................	$C_4 H_{10} O$	2·5573	0·4797	5·16	0·453	6·87
Ethyl Sulphide.........	$C_4 H_{10} S$	3·1101	0·4008	5·25	0·379	6·99
Ethyl Chloride.........	$C_2 H_5 Cl$	2·2269	0·2738	2·57	0·243	3·21
Ethyl Bromide.........	$C_2 H_5 Br$	3·7058	0·1896	2·96	0·171	3·76
Dutch Liquid...........	$C_2 H_4 Cl_2$	3·4174	0·2293	3·30	0·209	4·24
Aceton....................	$C_3 H_6 O$	2·0036	0·4125	3·48	0·378	4·50
Butyric Acid...........	$C_4 H_8 O_2$	3·0400	0·4008	5·13	0·378	6·82
Tri-chloride of Silicon	$Si Cl_3$	5·8833	0·1322	3·27	0·120	4·21
Tri-chloride of Phosphorus..............	$P Cl_3$	4·7464	0·1347	2·69	0·120	3·39
Tri-chloride of Arsenic	$As Cl_3$	6·2667	0·1122	2·96	0·101	3·77
Tetra-chloride of Titanium..............	$Ti Cl_4$	6·6402	0·1290	3·61	0·119	4·67
Tetra-chloride of Tin.	$Sn Cl_4$	8·9654	0·0939	3·54	0·086	4·59

§ 8. *Integration of the Differential Equations which express the first main Principle in the case of Gases.*

The differential equations deduced in sections 3 and 4, which in various forms express the first main principle of the Mechanical Theory of Heat in the case of gases, are not immediately integrable, as can be seen by inspection; and must therefore be treated after the method developed in § 3 of the Introduction. In other words, the integration becomes possible as soon as we subject the variables occurring in the equation to some one condition, thus determining the path of the change of condition of the body. We shall here give only two very simple examples of the process, the results of which are important for our further investigations.

Example 1. The gas changes its volume at Constant Pressure, and the quantity of heat required for such change is known.

In this case we select from the above equations one which contains p and v as independent variables, e.g. the last of Equations (15), which is

$$dQ = \frac{C_p - R}{R} vdp + \frac{C_p}{R} pdv.$$

As the pressure p is to be constant, we put $p = p_1$, and $dp = 0$; the equation then becomes

$$dQ = \frac{C_p}{R} p_1 dv,$$

which gives on integration (if we call v_1 the original value of v)

$$Q = \frac{C_p}{R} p_1 (v - v_1) \quad \text{..............(40).}$$

Example 2. The gas changes its volume at Constant Temperature, and the quantity of heat required for such change is known.

In this case we select an equation which contains T and v as independent variables, e.g. Equation (11), which is

$$dQ = C_v dT + \frac{RT}{v} dv.$$

As T is to be constant, we put $T=T_1$, and $dT=0$; whence we have

$$dQ = RT_1 \frac{dv}{v}.$$

Integrating,

$$Q = RT_1 \log \frac{v}{v_1} \text{.....................} (41).$$

Hence is derived the Principle that *if a Gas changes its volume without change of temperature, the quantities of heat absorbed or given off form an arithmetical series, while the volumes form a geometrical series.*

Again, if we put for R its value $\frac{p_1 v_1}{T_1}$, we have

$$Q = p_1 v_1 \log \frac{v}{v_1} \text{.....................} (42).$$

If we suppose this equation to refer, not directly to a unit weight of the gas, but to a quantity of it such that at pressure p it assumes a volume v_1, and then suppose that this volume changes under constant temperature to v, then the equation contains nothing which depends on the special nature of the gas. Therefore the quantity of heat absorbed is *independent of the nature of the gas.* Further, it does not depend on the temperature, but only on the pressure, being proportional to the original pressure.

Another application of the differential equations deduced in sections 3 and 4 consists in making some assumption as to the heat to be imparted to the gas during its change of condition, and then enquiring what course the change of condition will take under such circumstances. The simplest and at the same time most important assumption of this kind is that *no heat whatever is imparted to or taken from the gas during its change of condition.* For this purpose we may imagine the gas confined in a vessel impermeable to heat, or that the change is so rapid that no appreciable heat can pass to or from the gas in the time.

On this assumption we must put $dQ=0$. Let us do this for the three Equations (16). Then the first of these becomes

$$C_v dT + (C_p - C_v)\frac{T}{v}dv = 0.$$

Dividing by $T \times C_v$, and as before denoting $\frac{C_p}{C_v}$ by k, we have

$$\frac{dT}{T} + (k-1)\frac{dv}{v} = 0.$$

Integrating,

$$\log T + (k-1)\log v = \text{Const.}$$

or

$$Tv^{k-1} = \text{Const.}$$

If T_1, v_1 are the original values of T, v, we may eliminate the Constant, and obtain

$$\frac{T}{T_1} = \left(\frac{v_1}{v}\right)^{k-1} \text{........................(43).}$$

If this equation be applied for example to atmospheric air, then, writing $k = 1{\cdot}410$, we can easily calculate the change of temperature which corresponds to any given change of volume. If e.g. we assume a certain quantity of air to be taken at freezing temperature and at any pressure whatever, and to be compressed, either in a vessel impermeable to heat, or with great rapidity, to half its volume, then $T_1 = 273$ (absolute temperature) and $\frac{v_1}{v} = 2$; hence the equation becomes

$$\frac{T}{273} = 2^{0{\cdot}410} = 1{\cdot}329,$$

whence

$$T = 273 \times 1{\cdot}329 = 363,$$

or if t be the temperature measured in degrees above freezing point,

$$t = T - 273 = 90^\circ.$$

If a similar calculation is made for the compression of the gas to $\frac{1}{4}$ and $\frac{1}{10}$ of its original volume, results are obtained, which, combined with the former, are presented in the following Table.

Value of $\frac{v}{v_1}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{10}$
$\frac{T}{273}$	1·329	1·765	2·570
T	363	482	702
t	90°	209°	429°

Again, if in the second of equations (16) we put $dQ=0$, we get:

$$C_p dT + (C_v - C_p)\frac{T}{p}\,dp = 0.$$

This equation is of the same form as the last, except that p is in the place of v, and that C_p and C_v have their places interchanged. Hence in exactly the same way we shall obtain,

$$\frac{T}{T_1} = \left(\frac{p_1}{p}\right)^{\frac{1}{k}-1},$$

whence
$$\left(\frac{T}{T_1}\right)^k = \left(\frac{p_1}{p}\right)^{k-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (44).$$

Finally the last of Equations (16), if dQ be put $=0$, passes into the form already treated in § 5:

$$\frac{C_v}{C_p - C_v}\,vdp + \frac{C_p}{C_p - C_v}\,pdv = 0\,;$$

which may be written

$$\frac{dp}{p} + k\frac{dv}{v} = 0,$$

and gives on integration

$$\frac{p}{p_1} = \left(\frac{v_1}{v}\right)^k \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (45).$$

§ 9. *Determination of the External Work done during the change of volume of a gas.*

There is one quantity connected with the expansion of a gas which still requires to be specially considered, viz. the External Work done in the process. The element of this work, as determined in Equation (6), Ch. I, is

$$dW = pdv.$$

This work may be very clearly set forth by a graphic representation. We will adopt a rectangular system of co-ordinates, in which the abscissa represents the volume v, and the ordinate the pressure p. If we now suppose p to be expressed as a function of v, say $p = f(v)$, then this equation is the equation to a curve, whose ordinates express the values of p corresponding to the different values of v, and which for brevity we will call the Pressure-curve. In Fig. 3 let *rs* be this curve, so that, if *oe* represent the volume v existing at a certain instant, the ordinate *ef* drawn at *e* will represent the pressure at the same instant. If further *eg* represent an indefinitely small element of volume dv, and the ordinate *gh* is drawn at g, then we shall have an indefinitely small parallelogram *efhg*, whose area represents the external work done in an indefinitely small expansion of the body; and which differs from the product pdv only by an indefinitely small quantity of the second order, which may be neglected. The same holds for any other indefinitely small expansion; and hence in the case of a finite expansion (say from the volume v_1, represented by the abscissa *oa*, to that of v_2, represented by the abscissa *oc*) the external work, for which we have the equation

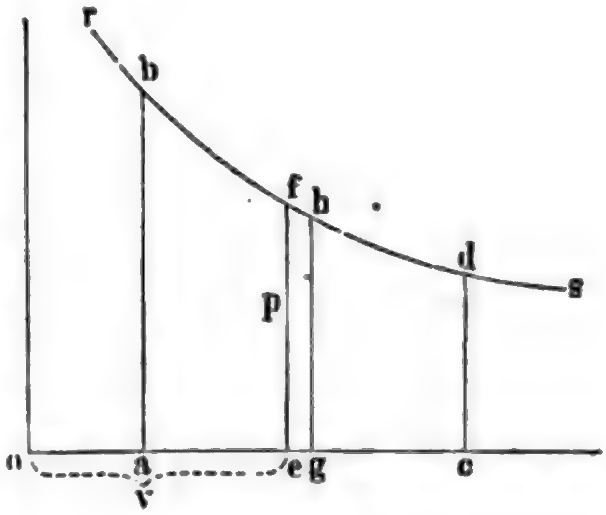

Fig. 3.

$$W = \int_{v_1}^{v_2} pdv \dots\dots\dots\dots\dots\dots (46),$$

is represented by the quadrangular figure *abdc*, which is bounded by the difference of abscissæ *ac*, the ordinates *ab* and *cd*, and the portion of the pressure-curve *bd*.

In order actually to perform the integration in equation (46) we must know the function of v which expresses the pressure p. On this point we will select as examples the cases already treated in § 8.

First, let us assume that the Pressure p is constant. Then the curve of pressure is a straight line parallel to the axis of x, and *abdc* is a rectangle (see Fig. 4) whose area is equal to the product of *ac* and *ab*. In this case then we obtain from (46), denoting the constant pressure by p_1,

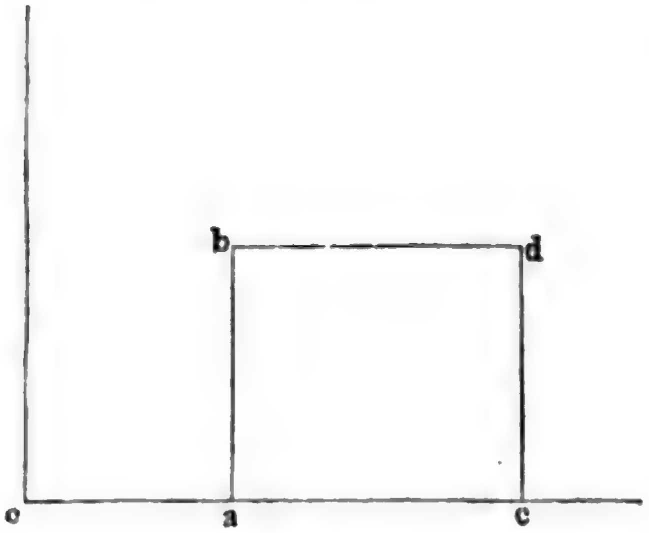

Fig. 4.

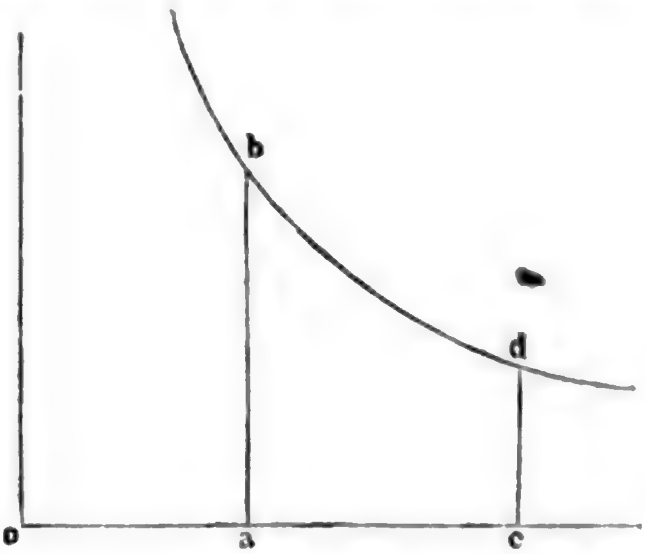

Fig. 5.

$$W = p_1 (v_2 - v_1) \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots (47).$$

Secondly, let us assume that the Temperature remains constant during the expansion of the gas. Then the law of Mariotte holds for the relation between pressure and volume, and is expressed by the equation

$$pv = \text{const.}$$

From the form of this equation we see that the curve of pressure is an equilateral hyperbola (Fig. 5) having the axes of co-ordinates as asymptotes. A pressure-curve of this kind, which involves the special condition that the temperature is constant, is usually called an Isothermal Curve.

To effect the integration in this case we may write for p

the value $\frac{p_1v_1}{v}$, where p_1v_1 is any value obtained for the constant in the above equation; we then get from (46):

$$W = p_1v_1\int_{v_1}^{v_2}\frac{dv}{v} = p_1v_1 \log\frac{v_2}{v_1} \;\ldots\ldots\ldots\ldots\; (48).$$

We observe that this value of W coincides with that given in equation (42) for Q; the reason for this being that the gas, while expanding at constant temperature, absorbs only so much heat as is required for the external work.

Joule has employed the equation (48) in one of his determinations of the Mechanical Equivalent of Heat. For this purpose he forced atmospheric air into a strong receiver, up to ten or twenty times its normal density. The receiver and pump were meantime kept under water, so that all the heat which was developed in pumping could be measured in the water. The apparatus is represented in Fig. 6, in which R is the receiver, and C the pump. The vessel G, as will be easily understood, was used for the drying of the air, and the vessel with the spiral tube served to give to the air, before its entrance into the pump, an exactly known temperature. From the total quantity of heat given in the calorimeter Joule subtracted the part due to the friction of the pump, the amount of which he determined by working the pump for exactly the same length of time, and under the same mean pressure, but without allowing the entrance of air, and then observing the heat produced. The remainder, after this was subtracted, he took as being the quantity of heat developed by the compression of the air; and this he compared with the work required for the compression as given by equation (48). By this means he obtained as the mean of two series of experiments the value of 444 kilogrammetres as the Mechanical Equivalent of Heat.

This value, it must be admitted, does not agree very well with the value 424 obtained by the friction of water; the reason of which is probably to be found in the far larger sources of error attending experiments on air. Nevertheless at that time, when the fact that the work required for developing a given quantity of heat was equal under all circumstances was not yet placed on a firm basis, the agreement of the values found by such wholly different methods was close enough to aid considerably in the establishment of the principle.

As a third case of determination of work done, we may assume that the gas changes its volume within an envelope

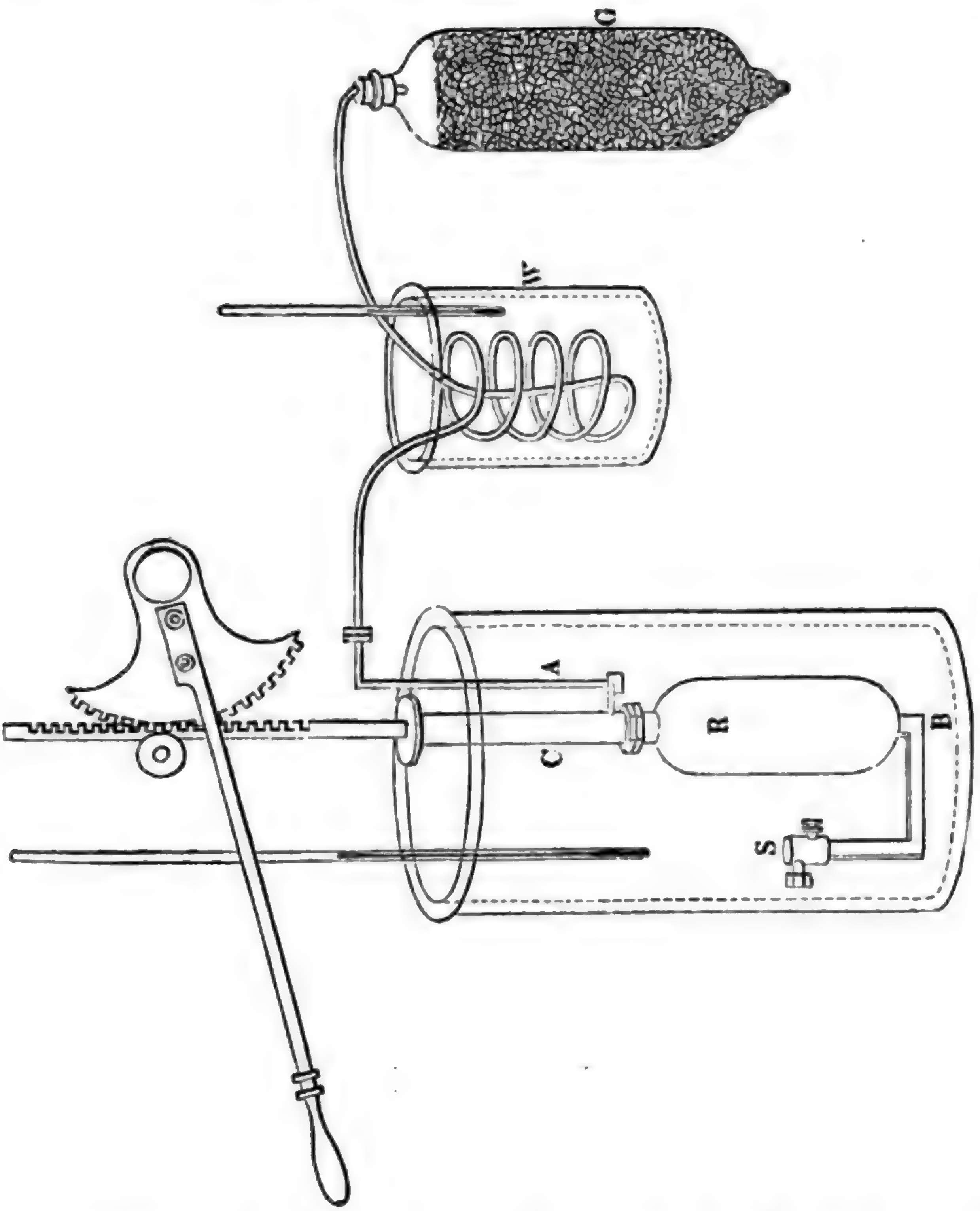

Fig. 6.

impermeable to heat; or, which comes to the same thing, that the change of volume takes place too rapidly to allow of the passing of any appreciable quantity of heat to or from the body during the time.

In this case the relation between pressure and volume is given by equation (45), viz.:

$$\frac{p}{p_1} = \left(\frac{v_1}{v}\right)^k.$$

The curve of pressure corresponding to this equation (Fig. 7) falls more steeply than that delineated in Fig. 5. Rankine has given to this special class of pressure-curves, which correspond to the case of expansion within an envelope impermeable to heat, the name of Adiabatic curves (from διαβαίνειν, to pass through). On the other hand Gibbs (*Trans. Connecticut Academy*, vol. II. p. 309) has proposed to name them Isentropic curves, because in this kind of expansion the Entropy, a quantity which will be discussed further on, remains constant. This latter form of nomenclature is the one which the author proposes to adopt, since it is both usual and advantageous to designate curves of this kind according to that quantity which remains constant during the action that takes place.

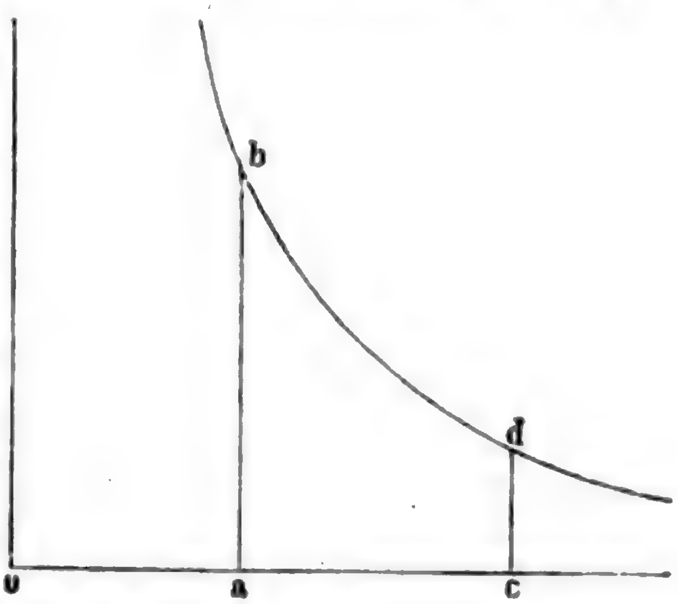

Fig. 7.

To effect the integration in this case, we may put, according to the above equation,

$$p = p_1 v_1^k \times \frac{1}{v^k};$$

whence (46) becomes

$$W = p_1 v_1^k \int_{v_1}^{v_2} \frac{dv}{v^k} = \frac{p_1 v_1^k}{k-1}\left(\frac{1}{v_1^{k-1}} - \frac{1}{v_2^{k-1}}\right),$$

or

$$W = \frac{p_1 v_1}{k-1}\left[1 - \left(\frac{v_1}{v_2}\right)^{k-1}\right] \dots\dots\dots\dots\dots (49).$$

CHAPTER III.

SECOND MAIN PRINCIPLE OF THE MECHANICAL THEORY OF HEAT.

§ 1. *Description of a special form of Cyclical Process.*

In order to prove and to make intelligible the second Principle of the Mechanical Theory of Heat, we shall commence by following out in all its parts, and graphically representing in the manner already described, one special form of cyclical process. For the latter purpose we will assume that the condition of the variable body is determined by its volume v and its pressure p, and will employ, as before, a rectangular system of co-ordinates, in which the abscissæ represent volumes, and the ordinates pressures. Any point on the plane of co-ordinates will then correspond to a certain condition of the body, in which its volume and pressure have the same volumes as the abscissa and ordinate of the point. Further, every variation of the body's condition will be represented by a line, whose extreme points determine the initial and final condition of the body, and whose form shews the way in which the pressure and volume have simultaneously varied.

In Fig. 8 let the initial condition of the body, at which the cyclical process commences, be given by the point a, so that the abscissa $oe = v_1$ and the ordinate $ea = p_1$ represent the initial volume and pressure respectively. By means of these two quantities the initial temperature, which we will call T_1, is also fixed.

Digitize

Now let the body in the first place expand, while retaining the same temperature T_1. If no heat were imparted to it during expansion, it would necessarily become cooler: we will therefore assume that it is put in communication with a body K, acting as a reservoir of heat, which body has the same temperature T_1, and does not appreciably vary from this during the cyclical process. From this body the variable body is supposed to draw during the expansion just sufficient heat to keep itself also at the temperature T_1.

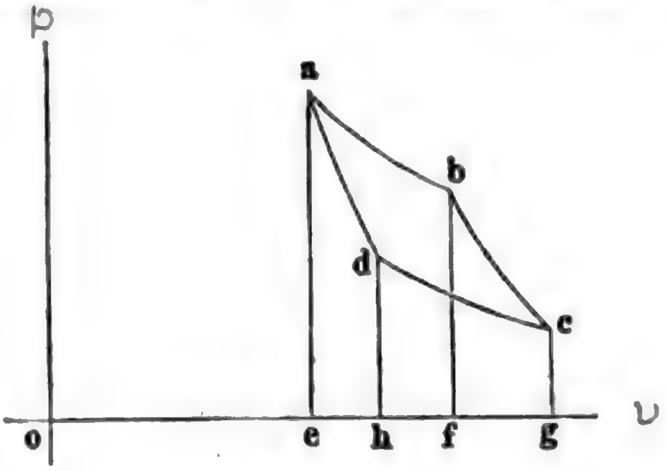

Fig. 8.

Clausius [illegible] p. 76

The curve, which during this expansion expresses the change of pressure, is part of an *isothermal* curve. In order that we may give definite forms to the graphic representations of this curve, and of others yet to be described, we will, without limiting the investigation itself to any particular bodies, draw the figure as it would appear in the case of a perfect gas. Then the isothermal curve, as explained above, will be an equilateral hyperbola; and, if the expansion take place from the volume $oe = v_1$ to the volume $of = V_1$, we shall obtain the part ab of such an equilateral hyperbola.

When the volume V_1 has been reached, let us suppose the body K_1 to be withdrawn, and let the variable body be left to continue its expansion by itself, without any heat being imparted to it. The temperature must then fall, and we obtain as curve of pressure an *isentropic* curve, which descends more steeply than the isothermal curve. Let this expansion continue till the volume V_2 is reached, giving us the portion of an isentropic curve bc. The lower temperature thus attained we may call T_2.

no further

From henceforward let the body be compressed, so as to bring it back to its original volume. Let the compression first take place at the constant temperature T_2, for which purpose we may suppose that the body is connected with a body K_2 at temperature T_2, acting as a reservoir of heat, and that it gives up to K_2 just so much heat as suffices to keep itself also at temperature T_2. The pressure-curve corresponding to this compression is again an isothermal curve, and in the special case of a perfect gas is another equilateral hyperbola, of which we obtain the portion *cd* during the reduction of volume to $oh = v_2$.

Finally, let the last compression, which brings the variable body back to its initial volume, take place without the presence of the body K_2, so that the temperature rises, and the pressure follows the line of an isentropic curve. We will assume that the volume $oh = v_2$, up to which the compression went on according to the first mode, is so chosen, that the compression which begins from this volume and continues to volume $oe = v_1$ is just sufficient to raise the temperature again from T_2 to T_1. If then the initial temperature is thus regained at the same time as the initial volume, the pressure must also return to its initial value, and the last curve of pressure must therefore exactly hit the point *a*. When the body is thus brought back again to the original condition, expressed by the point *a*, the cyclical process is complete.

§ 2. *Result of the Cyclical Process.*

During the two expansions which take place in the course of the cyclical process the external pressure must be overcome, and therefore external work must be *performed*; whereas conversely during the compressions external work is absorbed to perform them. These quantities of work are given directly by the figure, which is here reproduced. The work performed during the expansion *ab* is represented by the quadrangle *eabf*, and

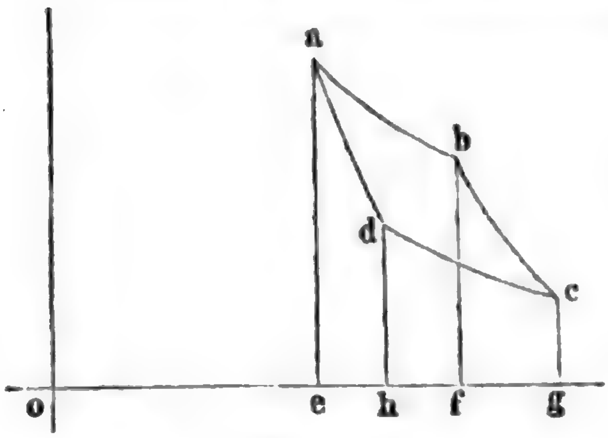

Fig. 9.

that performed during the expansion *bc* by the quadrangle *fbcg*. Again, the work absorbed for the compression *cd* is represented by the quadrangle *gcdh*, and that absorbed for the compression *da* by the quadrangle *hdae*. The two latter quantities, on account of the lower temperature which obtains during the compression, are smaller than the two former; and, if we subtract them from these, there remains an overplus of external work performed, which is represented by the quadrangle *abcd*, and which we will call *W*.

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To the external work thus gained must correspond, according to equation (5a) of Chapter I., a quantity Q, equal to it in value, which is required for its production. Now the variable body, during the first expansion, expressed by *ab*, which took place in connection with the body K_1, received from this latter a certain quantity of heat, which we may call Q_1; and again during the first compression, expressed by *cd*, which took place in connection with the body K_2, it imparted to this latter a certain quantity of heat, which may be called Q_2. During the second expansion *bc* and the second compression *da* the body neither imparted nor received heat. Now, since in the course of the whole cyclical process a certain quantity of heat Q is absorbed in work, it follows that the quantity of heat Q_1, received by the variable body, is larger than the quantity of heat Q_2 which it gives out, so that the difference $Q_1 - Q_2$ is equal to Q.

We may accordingly put

$$Q_1 = Q_2 + Q \qquad (1),$$

and can then distinguish in the quantity of heat Q_1, which the variable body has drawn from the body K_1, two parts, of which one Q is converted into work, whilst the other Q_2 is given back as heat into the body K_2. Since in all the other relations of the body the original condition is restored at the end of the cyclical process, and accordingly every variation which takes place at one part of the process is counterbalanced by an equal and opposite variation which takes place at some other part of the process, we may finally describe the result of the cyclical process in the following terms: *The one quantity of heat* Q, *derived from the body* K, *is transformed into work, and the other quantity* Q_2 *has passed over from the hotter body* K_1 *into the colder* K_2.

The whole of the cyclical process just described may also be supposed to take place in the reverse order. If we again begin with the conditions represented by the point a, in which the variable body has the volume v_1 and the temperature T_1, we may suppose that it first expands, without any heat being imparted to it, to the volume v_2, thus describing the curve ad, in which its temperature sinks from T_1 to T_2; that it is then connected with the body K_2, and expands at constant temperature T_2 from v_2 to V_2, describing the curve dc, during which it draws heat from the body K_2; that it then, without parting with its heat, is compressed from V_2 to V_1, describing the curve cb, during which its temperature rises from T_2 to T_1; finally that it is connected with the body K_2, at the constant temperature T_1, and whilst imparting its heat to K_1 is again compressed from V_1 to the initial volume v_1, describing the curve ba.

In this reversed process the quantities of work represented by the quadrangles $eadh$ and $hdcg$ are work performed or positive, those represented by $gcbf$ and $fbae$ are work absorbed or negative. The latter amount is larger than the former, and the remainder, as represented by the quadrangle $abcd$, is in this case work absorbed.

In addition the variable body has drawn the quantity of heat Q_2 from the body K_2, and has given out to the body K_1 the quantity of heat $Q_1 = Q_2 + Q$. Of the two parts of which Q_1 consists, the one Q corresponds to the work absorbed, and is generated from it, whilst the other Q_2 has passed over as heat from the body K_2 to the body K_1. Hence the result of the cyclical process may here be described as follows: the quantity of heat Q is generated out of work, and is given off to the body K_1, and the quantity of heat Q_2 has passed over from the colder body K_2 to the hotter body K_1.

§ 3. *Cyclical process in the case of a body composed partly of liquid, partly of vapour.*

In the foregoing sections, although in describing the cyclical process we made no assumptions limiting the nature of the variable body, yet the graphic representation of the process was made to correspond to the case of a perfect gas. It is perhaps as well therefore to examine the cyclical process over again in the case of a body of a different kind, in order to see how its appearance may vary with the nature of the body operated on. We will select for this examination a body which has not all its molecules in one and the same state in all its parts, but consists partly of liquid, partly of vapour at the maximum density.

Let us suppose a liquid contained in an expansible envelope, but only filling a part of it, and leaving the remainder free for vapour having the maximum density corresponding to the existing temperature T_1. The combined volumes of liquid and vapour are represented in Fig. 10 by the abscissa *oe*, and the pressure of the vapour by the ordinate *ea*. Now suppose the envelope to yield to the pressure and enlarge, while at the same time the liquid and vapour are connected with a body K_1 of constant temperature T_1. As the volume increases, more liquid becomes vaporised, but the heat consumed in the vaporisation is continually replaced from the body K_1, so that the temperature, and with it the pressure of the vapour, remains unaltered. The isothermal curve corresponding to this expansion is therefore a straight line parallel to the abscissa. When the combined volume has increased in this way from *oe* to *of*, a quantity of external work has been thereby performed, which is represented by the rectangle *eabf*. Now withdraw the body K_1, and let the envelope enlarge still further, without any passage of heat inwards or outwards. Then there will be partly an expansion of the vapour already existing, partly a generation of new vapour; in consequence the temperature will fall, and the pressure with it. Let this go on until the temperature has changed from T_1 to T_2, at which time the volume *og* has been attained. The fall of pressure, which has taken place during this expansion, will be represented by the isentropic curve *bc*, and the external work performed by *fbcg*.

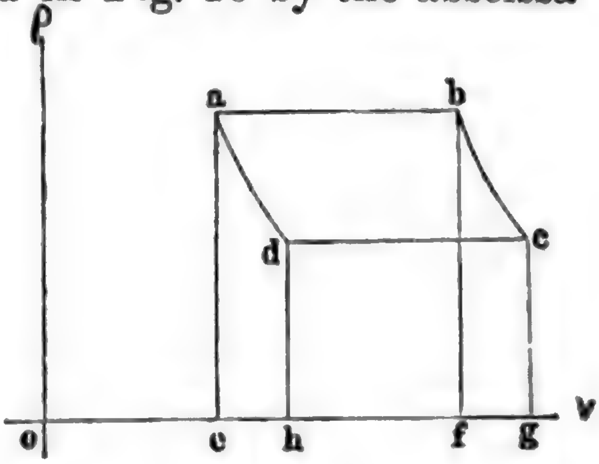

Fig. 10.

Now let the envelope be compressed, so as to bring the liquid and vapour back again to their original combined volume *oe*; and let this compression take place, partly in connection with the body K_2, of constant temperature T_2, to which all the heat produced by condensation of vapour passes over, so that the temperature T_2 remains unaltered: partly apart from this body, so that the temperature rises. Let it also be arranged, that the first compression shall extend only so far (to *oh*) as that the decrease of volume *he* then remaining may be just sufficient to raise the temperature again from T_2 to T_1. During this first compression the pressure remains unaltered, at the value *gc*; the external work thus absorbed is therefore represented by the rectangle *gcdh*. During the last compression the pressure increases, and is represented by the isentropic curve *da*, which must end exactly at the point *a*, since with the original temperature T_1 we must also have the original pressure *ea*. The external work absorbed in this last operation is represented by *hdae*.

At the end of the operation the liquid and vapour are again in their original condition, and the cyclical process is complete. The surplus of the positive above the negative external work, or the external work W which has been gained on the whole in the course of the process, is represented as before by the quadrangle *abcd*. To this work must correspond the absorption of an equivalent quantity of heat Q; and if we denote by Q_1 the heat imparted during the expansion, and by Q_2 the heat given out during the contraction, we may put $Q_1 = Q + Q_2$, and the final result of the cyclical process is again expressed by saying, that the quantity of heat Q is converted into work, and the quantity Q_2 has passed over from the hotter body K_1 to the colder K_2.

This cyclical process may also be carried out in the reverse direction, and then the quantity of heat Q will be generated out of work, and given off to the body K_1, while the quantity Q_2 will pass over from the colder body K_2 to the hotter K_1.

In a similar manner cyclical processes of this kind may be carried out with other variable bodies, and graphically represented by two isothermal and two isentropic lines; in which cases, while the form of the curves depends on the nature of the body, the result of the process is always of the same kind, viz. that one quantity of heat is converted into work, or generated out of work, and that another quantity passes over from a hotter to a colder body, or vice versâ.

The question now arises, *Whether the quantity of heat converted into work, or generated out of work, stands in a generally constant proportion to the quantity which passes over from the hotter to the colder body, or vice versâ; or whether the proportion existing between them varies according to the nature of the variable body, which is the medium of the transfer.*

§ 4. *Carnot's view as to the work performed during a Cyclical Process.*

Carnot, who was the first to remark that in the production of mechanical work heat passes from a hotter into a colder body, and that conversely in the consumption of mechanical work heat can be brought from a colder into a hotter body, and who also conceived the simple cyclical process above described (which was first represented graphically by Clapeyron), took a special view of his own as to the fundamental connection of these processes*.

In his time the doctrine was still generally prevalent that heat was a special kind of matter, which might exist within a body in greater or lesser quantity, and thereby occasion differences of temperature. In accordance with this doctrine it was supposed that heat might change the character of its distribution, in passing from one body into another, and further that it could exist in different conditions, which were denominated respectively 'free' and 'latent'; but that the whole quantity of heat existing in the universe could neither be increased nor diminished, inasmuch as matter can neither be created nor destroyed.

Carnot shared these views, (at the time [illegible] his writings) and accordingly treated it as self-evident that the quantities of heat, which the variable body in the course of the cyclical process receives from and gives out to the surrounding space, are equal to each other, and consequently cancel each other. He lays this down very distinctly in § 27 of his work, where he says: "we shall assume that the quantities of heat absorbed and emitted in these different transformations compensate each other exactly. This fact has never been held in doubt; admitted at first without reflection, it has since been verified in many instances by experiments with the calorimeter. To deny it would be to subvert the whole theory of heat, which rests on it as its basis."

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* *Reflexions sur la puissance motrice du feu.* Paris, 1824.

Now since on this assumption the quantity of heat existing in the body was the same after the cyclical process as before it, and yet a certain amount of work had been achieved, Carnot sought to explain this latter fact from the circumstance of the heat falling from a higher to a lower temperature. He drew a comparison between this descending passage of heat (which is especially striking in the steam-engine, where the fire gives off heat to the boiler, and conversely the cold water of the condenser absorbs heat) and the falling of water from a higher to a lower level, by means of which a machine can be set in motion, and work done. Accordingly in § 28, after making use of the expression 'fall of water,' he applies the corresponding expression 'fall of caloric' to the sinking of heat from a higher to a lower temperature.

Starting from these premises, he laid down the principle that the quantity of work done must bear a certain constant relation to the 'passage of heat,' i.e. the quantity of heat passing over at the time, and to the temperature of the bodies between which it passes; and that this relation is independent of the nature of the substance which serves as a medium for the performance of work and passage of heat. His proof of the necessary existence of this constant relation rests on the principle "That it is impossible to create moving force out of nothing," or in other words, "That perpetual motion is an impossibility."

This mode of dealing with the question does not accord with our present views, inasmuch as we rather assume that in the production of work a corresponding quantity of heat is consumed, and that in consequence the quantity of heat given out to the surrounding space during the cyclical process is less than that received from it. Now if for the production of work heat is consumed, then, whether at the same time with this consumption of heat there takes place the passage of another quantity of heat from a hotter to a colder body, or not, at least there is no ground whatever for saying that the work is created out of nothing. Accordingly not only must the principle enunciated by Carnot receive some modification, but a different basis of proof from that used by him must be discovered.

§ 5. *New Fundamental Principle concerning Heat.*

Various considerations as to the conditions and nature of heat had led the author to the conviction that the tendency of heat to pass from a warmer to a colder body, and thereby equalize existing differences of temperature (as prominently shewn in the phenomena of conduction and ordinary radiation), was so intimately bound up with its whole constitution that it must have a predominant influence under all conceivable circumstances. He thereupon propounded the following as a fundamental principle: "Heat cannot, of itself, pass from a colder to a hotter body."

The words 'of itself,' here used for the sake of brevity, require, in order to be completely understood, a further explanation, as given in various parts of the author's papers. In the first place they express the fact that heat can never, through conduction or radiation, accumulate itself in the warmer body at the cost of the colder. This, which was already known as respects direct radiation, must thus be further extended to cases in which by refraction or reflection the course of the ray is diverted and a concentration of rays thereby produced. In the second place the principle must be applicable to processes which are a combination of several different steps, such as e.g. cyclical processes of the kind described above. It is true that by such a process (as we have seen by going through the original cycle in the reverse direction) heat may be carried over from a colder into a hotter body: our principle however declares that simultaneously with this passage of heat from a colder to a hotter body there must either take place an opposite passage of heat from a hotter to a colder body, or else some change or other which has the special property that it is not reversible, except under the condition that it occasions, whether directly or indirectly, such an opposite passage of heat. This simultaneous passage of heat in the opposite direction, or this special change entailing an opposite passage of heat, is then to be treated as a *compensation* for the passage of heat from the colder to the warmer body; and if we apply this conception we may replace the words "of itself" by "without compensation," and then enunciate the principle as follows:

"A passage of heat from a colder to a hotter body cannot take place without compensation."

This makes it [illegible] heat [illegible]
a quantity. [illegible]

[illegible] glish [illegible] release.

This proposition, laid down as a Fundamental Principle by the author, has met with much opposition; but, having repeatedly had occasion to defend it, he has always been able to shew that the objections raised were due to the fact that the phenomena, in which it was believed that an uncompensated passage of heat from a colder to a hotter body was to be found, had not been correctly understood. To state these objections and their answers at this place would interrupt too seriously the course of the present treatise. In the discussions which follow, the principle, which, as the author believes, is acknowledged at present by most physicists as being correct, will be simply used as a fundamental principle; but the author proposes to return to it further on, and then to consider more closely the points of discussion which have been raised upon it.

§ 6. *Proof that the relation between the quantity of heat carried over, and that converted into work, is independent of the nature of the matter which forms the medium of the change.*

Assuming the foregoing principle to be correct, it may be proved that between the quantity of heat Q, which in a cyclical process of the kind described above is transformed into work (or, where the process is in the reverse order, generated by work), and the quantity of heat Q_2, which is transferred at the same time from a hotter to a colder body (or vice versâ), there exists a relation independent of the nature of the variable body which acts as the medium of the transformation and transfer; and thus that, if several cyclical processes are performed, with the same reservoirs of heat K_1 and K_2, but with different variable bodies, the ratio $\frac{Q}{Q_2}$ will be the same for all. If we suppose the processes so arranged, according to their magnitude, that the quantity of heat Q, which is transformed into work, has in all of them a constant value, then we have only to consider the magnitude of the quantity of heat Q_2 which is transferred, and the principle which is to be proved takes the following form: "If where two different variable bodies are used, the quantity of heat Q transformed into work is the same, then the quantity of heat Q_2, which is transferred, will also be the same." That is to say, supposing the two temperatures to [illegible]

Let there, if possible, be two bodies C and C' (e.g. the perfect gas and the combined mass of liquid and vapour, described above) for which the values of Q are equal, but those of the transferred quantities of heat are different, and let these different values be called Q_2 and Q'_2 respectively: Q'_2 being the greater of the two. Now let us in the first place subject the body C to a cyclical process, such that the quantity of heat Q is transformed into work, and the quantity Q_2 is transferred from K_1 to K_2. Next let us subject C' to a cyclical process of the reverse description, so that the quantity of heat Q is generated out of work, and the quantity Q'_2 is transferred from K_2 to K_1. Then the above two changes, from heat into work, and work into heat, will cancel each other; since we may suppose that when in the first process the heat Q has been taken from the body K_1 and transformed into work, this same work is expended in the second process in producing the heat Q, which is then returned to the same body K_1. In all other respects also the bodies will have returned, at the end of the two operations, to their original condition, with one exception only. The quantity of heat Q'_2, transferred from K_2 to K_1, has been assumed to be greater than the quantity Q_2 transferred from K_1 to K_2. Hence these two do not cancel each other, but there remains at the end a quantity of heat, represented by the difference $Q'_2 - Q_2$, which has passed over from K_2 to K_1. Hence a passage of heat will have taken place from a colder to a warmer body without any other compensating change. But this contradicts the fundamental principle. Hence the assumption that Q'_2 is greater than Q_2 must be false.

Again, if we make the opposite assumption, that Q'_2 is less than Q_2, we may suppose the body C' to undergo the cyclical process in the first, and C in the reverse direction. We then arrive similarly at the result that a quantity of heat $Q_2 - Q'_2$ has passed from the colder body K_2 to the hotter K_1, which is again contrary to the principle.

Since then Q'_2 can be neither greater nor less than Q_2 it must be equal to Q_2; which was to be proved.

We will now give to the result thus obtained the mathematical form most convenient for our subsequent reasoning. Since the quotient $\frac{Q}{Q_2}$ is independent of the nature of the variable body, it can only depend on the temperature of the two bodies K_1 and K_2, which act as heat reservoirs. The same will of course be true of the sum

$$1 + \frac{Q}{Q_2} = \frac{Q_2 + Q}{Q_2} = \frac{Q_1}{Q_2}.$$

This last ratio, which is that between the whole heat received and the heat transferred, we shall select for further consideration; and shall express the result obtained in this section as follows: "the ratio $\frac{Q_1}{Q_2}$ can only depend on the temperatures T_1 and T_2." This leads to the equation:

$$\frac{Q_1}{Q_2} = \phi\,(T_1 T_2) \ldots\ldots\ldots\ldots\ldots\ldots \text{(2)},$$

in which $\phi\,(T_1 T_2)$ is some function of the two temperatures, which is independent of the nature of the variable body.

§ 7. *Determination of the Function $\phi\,(T_1 T_2)$.*

The circumstance that the function given in equation (2) is independent of the nature of the variable body, offers a ready means of determining this function, since as soon as we have found its form for any single body it is known for all bodies whatsoever.

Of all classes of bodies the perfect gases are best adapted for such a determination, since their laws are the most accurately known. We will therefore consider the case of a perfect gas subjected to a cyclical process, similar to that graphically expressed in Fig. 8, § 1; which figure may be here reproduced (Fig. 11), inasmuch as a perfect gas was there taken as an example of the variable body. In this process the gas takes up a quantity of heat Q during its expansion *ab*, and gives out a quantity of heat Q_2 during its compression *cd*. These quantities we shall calculate, and then compare with each other.

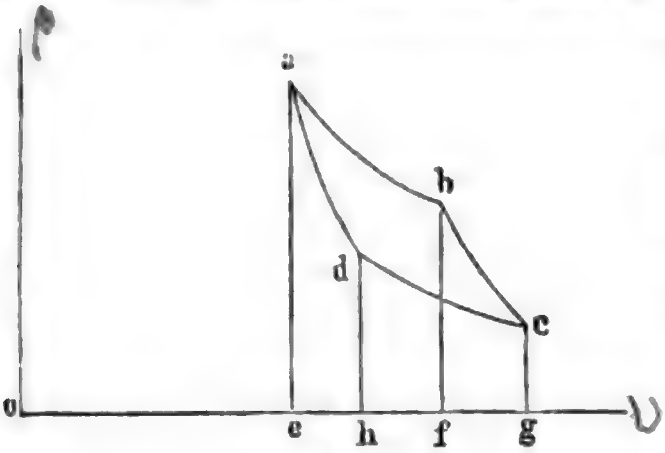


Fig. 11.

For this purpose we must first turn our attention to the volumes represented by the abscissæ *oe*, *oh*, *of*, *og*, and denoted by v_1, v_2, V_1, V_2, in order that we may ascertain the relation between them. Now the volumes $v_1 v_2$ (represented by *oe*, *oh*) form the limits of that change of volume to which the isentropic curve *ad* refers, and which may be considered at pleasure as an expansion or a compression. Such a change of volume, during which the gas neither takes in nor gives out any heat, has been treated of in § 8 of the last chapter, in which we arrived at the following equation (43), p. 62:

$$\frac{T}{T_1} = \left(\frac{v_1}{v}\right)^{k-1},$$

where T and v are the temperature and volume at any point in the curve. Substituting for these in the present case the final values T_2 and v_2, we have:

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1} \quad\ldots\ldots\ldots\ldots\ldots\ldots(3).$$

In exactly the same way we obtain for the change of volume represented by the isentropic curve *bc* (of which the initial and final temperatures are also $T_1 T_2$):

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{k-1} \quad\ldots\ldots\ldots\ldots\ldots\ldots(4).$$

Combining these two equations we obtain:

$$\frac{V_1}{V_2} = \frac{v_1}{v_2}, \text{ or } \frac{V_1}{v_1} = \frac{V_2}{v_2} \ldots\ldots\ldots\ldots\ldots\ldots(5).$$

We must now turn to the change of volume represented by the isothermal curve *ab*, which takes place at the constant temperature T_1, and between the limits of volume v_1 and V_1. The quantity of heat received or given off during such a change of volume has been determined in § 8 of the last chapter, and by the equation (41) there given, p. 61, we may put in the present case:

$$Q_1 = RT_1 \log \frac{V_1}{v_1} \ldots\ldots\ldots\ldots\ldots\ldots(6).$$

Similarly for the change of volume represented by the isothermal curve *dc*, which takes place at temperature T_2 between the limits of volume v_2 and V_2, we have:

$$Q_2 = RT_2 \log \frac{V_2}{v_2} \ldots\ldots\ldots\ldots\ldots\ldots \text{(7)}.$$

From these two equations we obtain by division:

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(8)},$$

since by (5) $$\frac{V_1}{v_1} = \frac{V_2}{v_2}.$$

The function occurring in equation (2) is now determined, since to bring this equation into unison with the last equation (8) we must have:

$$\phi\,(T_1 T_2) = \frac{T_1}{T_2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(9)}.$$

We can now use in place of equation (2) the more determinate equation (8), which may also be written as follows:

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(10)}.$$

The form of this equation may be yet further changed, by affixing positive and negative signs to Q_1, Q_2. Hitherto these have been treated as absolute quantities, and the distinction that the one represents heat taken in, the other heat given out, has been always expressed in words. Let us now for convenience agree to speak of heat taken in only, and to treat heat given out as a negative quantity of heat taken in. If accordingly we say that the variable body has taken in during the cyclical process the quantities of heat Q_1 and Q_2, we must here conceive Q_2 as a negative quantity, i.e. the same quantity which has hitherto been expressed by $-Q_2$. On this supposition equation (10) becomes:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(11)}.$$

§ 8. *Cyclical processes of a more complicated character.*

Hitherto we have confined ourselves to cyclical processes in which the taking in of quantities of heat, positive or negative, takes place at two temperatures only. Such processes we shall in future call for brevity's sake Simple Cyclical Processes. But it is now time to treat of cyclical processes, in which the taking in of positive and negative quantities of heat takes place at more than two temperatures.

We may first consider a cyclical process with heat taken in at three temperatures. This is represented graphically by the figure *abcdefa* (Fig. 12), which, as in the former cases, consists of isentropic and isothermal curves only. These curves are again drawn, by way of example, in the form which they would take in the case of a perfect gas, but this is not essential. The curve *ab* represents an expansion at constant temperature T_1; *bc* an expansion without taking in heat, during which the temperature falls from T_1 to T_2; *cd* an expansion at constant temperature T_2; *de* an expansion without taking in heat, during which the temperature falls from T_2 to T_3; *ef* a compression at constant temperature T_3; and lastly *fa* a compression without taking in heat, during which the temperature rises from T_3 to T_1, and which brings back the variable body to its exact original volume. In the

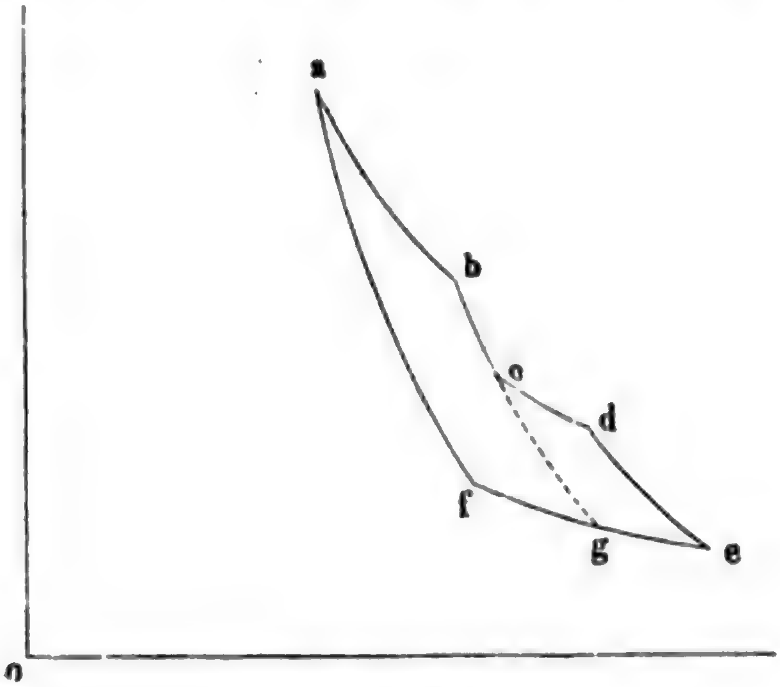


Fig. 12.

expansions *ab* and *cd* the variable body takes in positive quantities of heat Q_1 and Q_2, and in the compression *ef* the negative quantity of heat Q_3. It now remains to find a relation between these three quantities.

For this purpose let us suppose the isentropic curve *bc* produced in the dotted line *cg*. The whole process is thereby divided into two Simple Processes *abgfa* and *cdegc*. In the first the body starts from the condition *a* and returns to the same again. In the second we may suppose a body of the same nature to start from the condition *e*, and to return to the same again. The negative quantity of heat Q_3, which is taken in during the compression *ef*, we may suppose divided into two parts q_3 and q_3', of which the first is taken in during the compression *gf*, and the second during the compression *eg*. We can now form the two equations, corresponding to equation (11), which will hold for the two simple processes. These equations are, for the process *abgfa*,

$$\frac{Q_1}{T_1}+\frac{q_3}{T_3}=0,$$

and for the process *cdegc*

$$\frac{Q_2}{T_2}+\frac{q_3'}{T_3}=0.$$

Adding these equations we obtain

$$\frac{Q_1}{T_1}+\frac{Q_2}{T_2}+\frac{q_3+q_3'}{T_3}=0\ ;$$

or, since $$q_3+q_3'=Q_3,$$

$$\frac{Q_1}{T_1}+\frac{Q_2}{T_2}+\frac{Q_3}{T_3}=0 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots (12).$$

In exactly the same way we may treat a process in which heat is taken in at four temperatures, as represented by the annexed figure *abcdefgha*, Fig. 13, which again consists solely of isentropic and isothermal lines. The expansions *ab* and *cd*, and the compressions *ef* and *gh*, take place at temperatures T_1, T_2, T_3, T_4, and during these times the quantities of heat Q_1, Q_2, Q_3, Q_4 are taken in respectively; the two former being positive, and the two latter negative. Produce the isentropic curves *bc* and *fg* in the dotted lines *ci* and *gk* respectively. Then the whole process is subdivided into three Simple Processes *akgha, kbifk,* and *cdeic,* which may be supposed to be

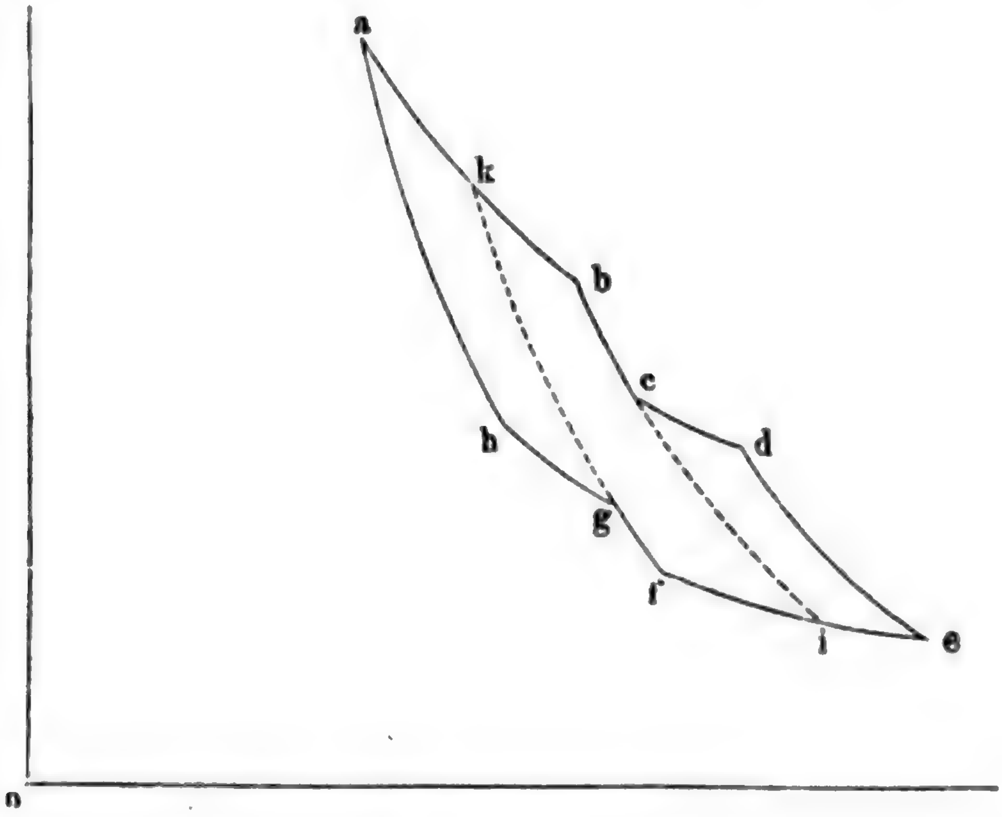


Fig. 13.

carried out with three exactly similar bodies. We may suppose the quantity of heat Q_1, taken in during the expansion *ab*, to be divided into two parts q_1 and q_1', corresponding to expansions *ak* and *kb*; and the negative quantity Q_2, taken in during the compression *ef*, to be likewise divided into q_2 and q_2', corresponding to compressions *if* and *ci*. Then we can form the following equations for the three simple processes: First, for *akgha*

$$\frac{q_1}{T_1} + \frac{Q_4}{T_4} = 0.$$

Secondly, for *kbifk*

$$\frac{q_1'}{T_1} + \frac{q_2}{T_2} = 0.$$

Thirdly, for *cdeic*

$$\frac{Q_3}{T_3} + \frac{q_2'}{T_2} = 0.$$

Adding, we obtain

$$\frac{q_1+q_1'}{T_1}+\frac{Q_2}{T_2}+\frac{q_3+q_3'}{T_3}+\frac{Q_4}{T_4}=0,$$

or

$$\frac{Q_1}{T_1}+\frac{Q_2}{T_2}+\frac{Q_3}{T_3}+\frac{Q_4}{T_4}=0 \quad \text{..................}(13).$$

In exactly the same way any other cyclical process, which can be represented by a figure consisting solely of isentropic and isothermal lines, and which has any given number of temperatures at which heat is taken in, may be made to yield an equation of the same form, viz.

$$\frac{Q_1}{T_1}+\frac{Q_2}{T_2}+\frac{Q_3}{T_3}+\frac{Q_4}{T_4}+\ldots\ldots=0,$$

or generally

$$\Sigma\frac{Q}{T}=0 \quad \text{......................}(14).$$

§ 9. *Cyclical Processes, in which taking in of Heat and change of Temperature take place simultaneously.*

We have lastly to consider such cyclical processes as are represented by figures not consisting solely of isentropic and isothermal lines, but altogether general in form.

The mode of treatment is as follows. Let point *a* in

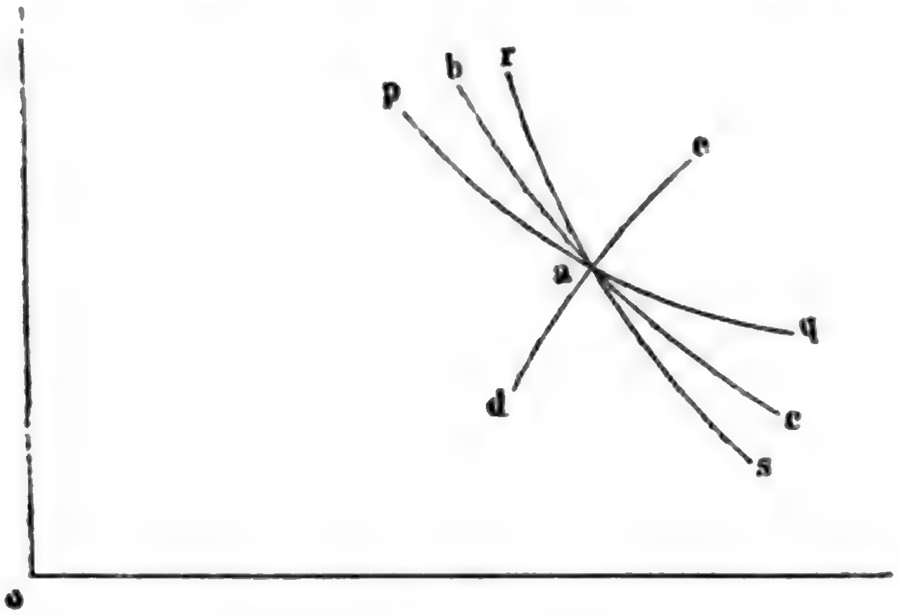


Fig. 14.

Fig. 14 represent any given condition of the variable body; let *pq* be an arc of the isothermal curve which passes through *a*, *rs* an arc of the isentropic curve which passes through the same point. Now let the body undergo a variation which is expressed by a pressure-curve not coinciding with either of the above, but taking some other course such as *bc* or *de*. Then we may consider such a variation as made up of a very great number of very small variations, in which we have alternately change of temperature without taking in of heat, and taking in of heat without change of temperature. This series of successive variations will be represented by a discontinuous line, made up of alternate elements of isothermal and isentropic curves, as drawn in Fig. 15, along the course of *bc* and *de*. The smaller the elements of which the discontinuous curve is made up, the more closely will it coincide with the continuous line, and if these are indefinitely small the coincidence will be indefinitely close. In this case it can only make an indefinitely small difference, in relation to the quantities of heat taken in and their temperatures, if we substitute for the variation represented by the continuous line the indefinitely large number of alternating variations, which are represented by the discontinuous line.

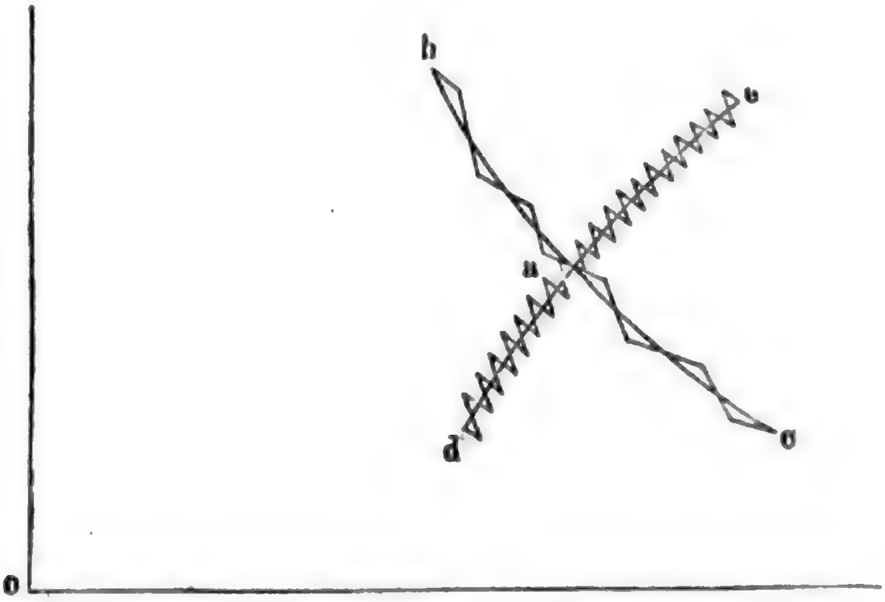


Fig. 15.

We are now in a position to consider a complete cyclical process, in which the taking in of heat is simultaneous with changes of temperature, and which may be represented graphically by curves of any form whatever, or merely by a single continuous and closed curve, such as is drawn in Fig. 16. The area of this closed curve represents the external work consumed. Let it be divided into indefinitely thin strips by means of adjacent isentropical curves, as shewn by the dotted lines in Fig. 16. Let us suppose these curves joined at the top and bottom by indefinitely small elements

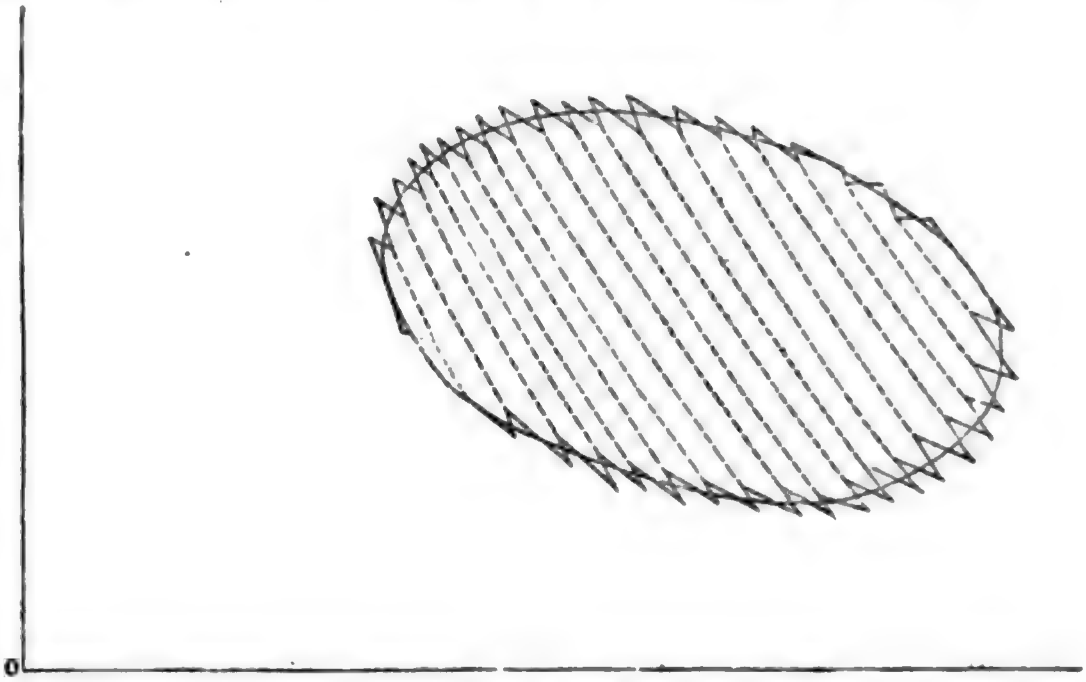


Fig. 16.

of isothermal lines, which cut the given curve, so that throughout its length we have a broken line, which is everywhere in indefinitely close coincidence with it. By the above reasoning we may substitute for the process represented by the continuous line the other process represented by the broken line, without producing any perceptible alteration in the quantities of heat taken in, or in their temperatures. Further, we may again substitute for the process represented by the broken line an indefinitely great number of Simple Processes, which will be represented by the indefinitely small quadrangular strips, made up each of two adjacent isentropic curves, and two indefinitely small elements of isothermal curves. If then for each one of these last processes we form an equation similar to (11), in which the two quantities of heat are indefinitely small, and can therefore be denoted by differentials of Q; and if all these equations be finally added together; we shall then obtain an equation of the same form as (14), but in which the sign of summation is replaced by the sign of Integration, thus:

$$\int \frac{dQ}{T} = 0 \quad \text{.......................} (15).$$

This equation, which was first published by the author in 1854 (Pogg. *Ann.* vol. 93, p. 500), forms a very convenient expression for the second main Principle of the Mechanical Theory of Heat, as far as it relates to reversible processes. This Principle may be expressed in words as follows: *If in a reversible Cyclical Process every element of heat taken in (positive or negative) be divided by the absolute temperature at which it is taken in, and the differential so formed be integrated for the whole course of the process, the integral so obtained is equal to zero.*

If the integral $\int\frac{dQ}{T}$, corresponding to any given succession of variations of a body, be always equal to zero provided the body returns finally to its original condition, whatever the intervening conditions may be, then it follows that the expression under the integral sign, viz. $\frac{dQ}{T}$, must be the perfect differential of a quantity, which depends only on the present condition of the body, and is altogether independent of the way in which it has been brought into that condition. If we denote this quantity by S, we may put

$$\frac{dQ}{T} = dS,$$

or

$$dQ = TdS \text{ ....} \quad \text{(VI)},$$

an equation which forms another expression, very convenient in the case of certain investigations, for the second main principle of the Mechanical Theory of Heat.

Since, by Avogadro's Law, the temperature is the average heat of an independently moving part (or molecule)

$$\frac{dQ}{T} = \frac{N\,dQ}{Q} \quad \text{and} \quad \int\frac{dS}{T} = \int N\,d\log Q$$

[illegible]

CHAPTER IV.

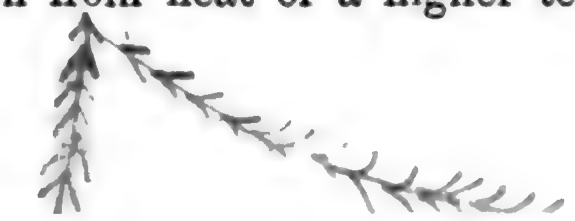
THE SECOND MAIN PRINCIPLE UNDER ANOTHER FORM, OR PRINCIPLE OF THE EQUIVALENCE OF TRANSFORMATIONS.

§ 1. *On the two different kinds of Transformations.*

In the last chapter it was shewn that in a Simple Cyclical Process two variations in respect to heat take place, viz. that a certain quantity of heat is converted into work (or generated out of work), and another quantity of heat passes from a hotter into a colder body (or vice versâ). It was found further that between the quantity of heat transformed into work (or generated out of work) and the quantity of heat transferred, there must be a definite relation, which is independent of the nature of the variable body, and therefore can only depend on the temperatures of the two bodies which serve as reservoirs of heat.

For the former of these two variations we have already employed the word "transformation," inasmuch as we said, when work was expended and heat thereby produced, or conversely when heat was expended and work thereby produced, that the one had been "transformed" into the other. We may use the word "transformation" to express the second variation also (which consists in the passage of heat from one body into another, which may be colder or hotter than the first), inasmuch as we may say that heat of one temperature "transforms" itself into heat of another temperature.

On this principle we may describe the result of a simple cyclical process in the following terms: Two transformations are produced, a transformation from heat into work (or vice versâ) and a transformation from heat of a higher tempera-



ture to heat of a lower (or vice versâ). The relation between these two transformations is therefore that which is to be expressed by the second Main Principle.

Now, in the first place, as concerns the transformation of heat at one temperature to heat at another, it is evident at once that the two temperatures, between which the transformation takes place, must come under consideration. But the further question now arises, whether in the transformation from work into heat, or from heat into work, the temperature of the particular quantity of heat concerned plays an essential part, or whether in this transformation the particular temperature is matter of indifference.

If we seek to deduce the answer to this question from the consideration of a Simple Cyclical Process, as described above, we find that it is too limited for our purpose. For since in this process there are only two bodies which act as heat reservoirs, it is tacitly assumed that the heat which is transformed into work is derived from (or conversely the heat generated out of work is taken in by) one or other of these same two bodies, between which the transference of heat also takes place. Hence a definite assumption is made from the beginning as to the temperature of the heat transformed into work (or conversely generated out of work), viz. that it coincides with one of the two temperatures at which the transference of heat takes place; and this limitation prevents us from learning what influence it would have on the relation between the two transformations if the first-mentioned temperature were to alter, while the two latter remained unaltered.

To ascertain this influence, we may revert to those more complicated cyclical processes, which have also been described in the last chapter, § 8, and to the equations derived from them. But in order to give a clearer and simpler view of the question it is better to consider a single process specially chosen for this investigation, and by its help to bring out the second Main Principle anew in an altered form.

§ 2. *On a Cyclical Process of special form.*

Let us again take a variable body, whose condition is completely determined by its volume and pressure, so that we can represent its variations graphically in the manner already described. We will once more by way of example construct the figure in the form it assumes for a perfect gas, but without making in the investigation itself any limiting assumption whatever as to the nature of the body.

Let the body be first taken in the condition defined by the point *a* in Fig. 17, its volume being given by the abscissa

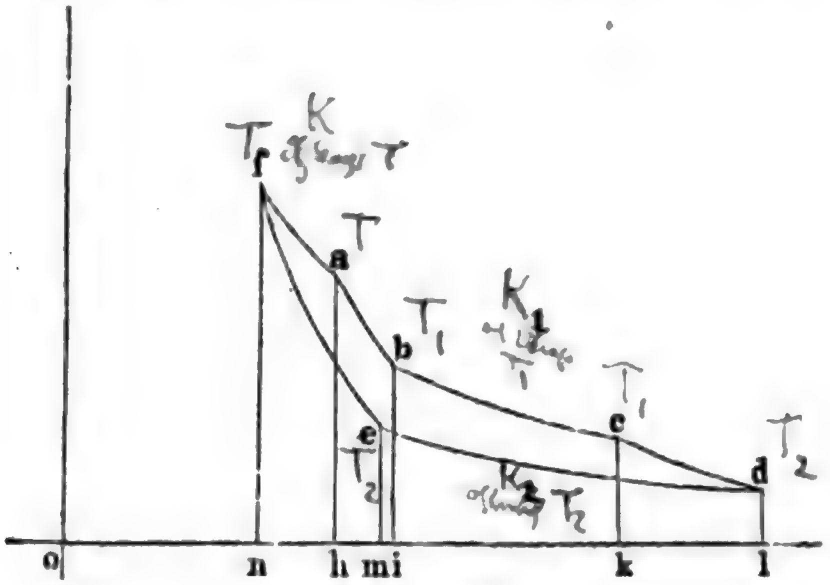


Fig. 17.

oh, and its pressure by the ordinate *ha*. Let *T* be the temperature corresponding to these two quantities, and determined by them. We will now subject the body to the following successive variations:

(1) The temperature *T* of the gas is changed to T_1, which we will suppose less than *T*. This may be done by enclosing the gas within a non-conducting envelope, so that it can neither take in nor give out heat, and then allowing it to expand. The decrease of pressure caused by the simultaneous increase of volume and fall of temperature will be represented by the isentropic curve *ab*; so that, when the temperature of the gas has reached T_1, its volume and pressure have become *oi* and *ib* respectively.

(2) The variable body is placed in communication with a body K_1 of temperature T_1, and then allowed to expand still further, but so that all the heat lost in expansion is restored by K_1. With respect to the latter it is assumed that, on account of its magnitude or from some other cause, its temperature is not

[illegible] must be altered, by some definite change of state, though not in temp.–

perceptibly altered by this giving out of heat, and may therefore be taken as constant. Hence the variable body will also preserve during its expansion the same constant temperature T_1, and its diminution of pressure will be represented by an isothermal curve *bc*. Let the quantity of heat thus given off by K_1 be called Q_1.

(3) The variable body is disconnected from K_1 and allowed to expand still further, without being able either to take in or give out heat, until its temperature has fallen from T_1 to T_2. Let this diminution of pressure be represented by the isentropic curve *cd*.

(4) The variable body is placed in communication with a body K_2, of constant temperature T_2, and is then compressed, parting with all the heat generated by the compression to K_2. This compression goes on until K_2 has received the same quantity of heat Q_1, as was formerly abstracted from K_1. In this case the pressure increases according to the isothermal curve *de*.

(5) The variable body is disconnected from K_2, and compressed, without being able to take in or give out heat, until its temperature has risen from T_2 to its original value T, the pressure increasing according to the isentropic curve *ef*. The volume *on*, to which the body is brought by this process, is less than the original volume *oh*, since the pressure to be overcome, and consequently the external work to be transformed into heat, is less during the compression *de* than during the expansion *bc*; so that, in order to restore the same quantity of heat Q_1, the compression must be continued further than would have been necessary merely to annul the expansion.

(6) The variable body is placed in communication with a body K of constant temperature T, and allowed to expand to its original volume *oh*, the heat lost in expansion being restored from K. Let Q be the quantity of heat thus required. If the body attains the original volume *oh* at the original temperature T, then the pressure must also revert to its original value, and the isothermal curve, which represents this last expansion, will therefore terminate exactly in the point *a*.

The above six variations make up together a Cyclical Process, since the variable body is finally restored exactly to its original condition. Of the three bodies, K, K_1, K_2, which in the whole process only come under consideration in so far as they serve as sources or reservoirs of heat, the two first have at the end lost the quantities of heat Q, Q_1 respectively, whilst the last has gained the quantity of heat Q_1; this may be expressed by saying that Q_1 has passed from K_1 to K_2, while Q has disappeared altogether. This last quantity of heat must, by the first fundamental principle, have been transformed into external work. This gain of external work is due to the fact that in this cyclical process the pressure during expansion is greater than during compression, and therefore the positive work greater than the negative; its amount is represented, as is easily seen, by the area of the closed curve *abcdefa*. If we call this work W, we have by equation (5a) of Chapter I.

Much better [illegible] the [illegible] [illegible]

$$Q = W.$$

It is easily seen that the above Cyclical Process embraces as a special case the process treated of at the commencement of Chapter III., and represented in Fig. 8. For if we make the special assumption that the temperature T of the body K is equal to the temperature T_1 of the body K_1, we may then do away with K altogether, and use K_1 instead. The result of the process will then be that one part of the heat given out by the body K_1 has been transformed into work, and the other part has been transferred to the body K_2, just as was the case in the process above mentioned.

The whole of this cyclical process may also be carried out in the reverse order. The first step will then be to connect the variable body with K, and to produce, instead of the final expansion *fa* of the former case, an initial compression *af*: and similarly the expansions *fe* and *ed*, and the compressions *dc*, *cb*, and *ba* will be produced one after another, under exactly the same circumstances as the converse variations in the former case. It is obvious that the quantities of heat Q and Q_1 will now be *taken in* by the bodies K and K_1 respectively, and the quantity of heat Q_1 will be *given out* by the body K_2. At the same time the negative work is now greater than the positive, so that the area of the closed figure now represents a *loss* of work. The result of the reversed process is therefore that the quantity of heat Q_1 has been transferred from K_2 to K_1, and that the quantity of heat Q has been generated out of work and given to the body K.

§ 3. *On Equivalent Transformations.*

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In order to learn the mutual dependence of the two simultaneous transformations above described, viz. the transference of Q_1, and the conversion into work of Q, we shall first assume that the temperatures of the three reservoirs of heat remain the same, but that the cyclical processes, through which the transformations are effected, are different. This may be either because different variable bodies are subjected to similar variations, or because the same body is subjected to any other cyclical process whatever, subject only to the condition that the three bodies K, K_1 and K_2 are the only bodies which receive or give out heat, and also that of the two latter the one receives just as much as the other gives out. These different processes may either be reversible, as in the case considered, or non-reversible; and the law which governs the transformations will vary accordingly. However the modification which the law undergoes for non-reversible processes can be easily applied at a later period, and hence for the present we will confine ourselves to the consideration of reversible processes.

For all such it follows from the Principle laid down in the last chapter (p. 78) that the quantity of heat Q_1, transferred from K_1 to K_2, must stand in a constant relation to the quantity Q transformed into work. For let us suppose that there were two such processes, in which, while Q was the same in both, Q_1 was different: then we might successively execute that in which Q_1 was the smaller in the direct order, and the other in the reverse. In this case the quantity of heat Q, which in the first process would have been transformed into work, would in the second process be transformed again into heat and given back to the body K; and in other respects also everything would at the conclusion be restored to its original condition, with this single exception that the quantity of heat transferred from K_2 to K_1 in the second process, would be greater than the quantity transferred from K_1 to K_2 in the first process. Thus on the whole we have a transfer of heat from the colder body K_2 to the hotter K_1, with nothing to compensate for it. As this contradicts the fundamental principle, it follows that the above supposition cannot be true; in other words Q must always stand in the same ratio to Q_1.

Of the two transformations in a reversible process such as the above, either can replace the other, provided this latter be taken in the reverse direction: in other words, if a transformation of the one kind has taken place, this can be again reversed, and a transformation of the other kind substituted in its place, without the occurrence of any other permanent change. For example, let a quantity of heat Q be in any way generated out of work, and taken in by the body K; then by the cyclical process above described it can be again withdrawn from the body K, and transformed back into work, but in so doing a quantity of heat Q_2 will be transferred from the body K_1 to the body K_2. Again, if the quantity of heat Q_1 has previously passed from K_1 to K_2, it can by performing the above process in the reverse order be transferred back again to K_1, whilst at the same time the quantity of heat Q, at the temperature of the body K, will be generated out of work.

It is thus seen that these two kinds of transformation may be treated as processes of the same nature; and two such transformations, which may mutually replace each other in the way indicated, will be henceforth called "Equivalent Transformations."

§ 4. *Equivalence-Values of the Transformations.*

We have now to find the law according to which the above transformations must be expressed mathematically, so that the equivalence of the two may appear from the equality of their values. The mathematical value of a transformation may be termed, thus determined, its "Equivalence-Value."

We must first settle the order in which each transformation is to be taken as positive: this may be chosen arbitrarily for one of the two classes, but it will then be fixed for the other, since clearly we must regard a transformation in the latter class as positive, if it is equivalent to a positive transformation in the former. In all that follows we shall consider the transformation of Work into Heat, and therefore the passage of heat from a higher to a lower temperature, as being positive quantities. It will be seen later why this choice as to the positive and negative sign is preferable to the opposite.

With regard to the magnitude of the equivalence-value, it is at once seen that the value of a change from work into heat must be proportional to the quantity of heat generated, and that beyond this it can only depend on its temperature. We may therefore express generally the equivalence-value of the generation out of work of the quantity of heat Q, of temperature T, by the formula $Q \times f(T)$, where $f(T)$ is a function of temperature which is the same for all cases. If Q is negative in this formula, what is expressed is that the quantity of heat Q has been transformed, not out of work into heat, but out of heat into work.

Similarly the value of the passage of a quantity of heat Q from the temperature T_1 to the temperature T_2 must be proportional to the quantity of heat which passes, and beyond this can only depend on the two temperatures. We may therefore express it generally by the formula $Q \times F(T_1, T_2)$, in which $F(T_1, T_2)$ is a function of the two temperatures, also constant for all cases, and which we cannot at present determine more closely; but of which it is clear from the commencement that, if the two temperatures are interchanged, it must change its sign, without changing its numerical value. We may therefore write,

$$F(T_2, T_1) = -F(T_1, T_2) \ldots\ldots\ldots\ldots\ldots (1).$$

In order to compare these two expressions with each other, we have the condition that in every reversible process of the kind given above the two transformations that take place must be equal in magnitude but of opposite sign, so that their algebraical sum is zero. Thus if we choose for a moment the particular process fully described above (§ 2), the quantity of heat Q, at temperature T, is then transformed into work, giving as its equivalence-value $-Q \times f(T)$; and the quantity of heat Q_1 passes from temperature T_1 to T_2, thus giving as its equivalence-value $Q_1 \times F(T_1, T_2)$. Therefore the following equation must hold:

$$-Q \times f(T) + Q_1 \times F(T_1, T_2) = 0 \ldots\ldots\ldots\ldots (2).$$

Let us now suppose a similar process performed in the reverse order, and under the conditions that the bodies K_1

and K_2, and the quantity of heat Q_1 which passes between them, remain the same, but that for the body K of temperature T is substituted another body K' of temperature T': and let us call the heat generated out of work in this case Q'. Then, corresponding to the former equation, we have the following:

$$Q' \times f(T') + Q_1 \times F(T_2, T_1) = 0 \;\ldots\ldots\ldots\; (3).$$

Adding (2) and (3) and substituting from (1) we obtain,

$$-Q \times f(T) + Q' \times f(T') = 0 \;\ldots\ldots\ldots\ldots\; (4).$$

Now let us consider, as is clearly allowable, that these two successive processes make up together a single process; then in this latter the two transferences of heat between K_1 and K_2 will cancel each other and disappear from the result; we have therefore only left the transformation into work of the quantity of heat Q, given off by K, and the generation out of work of the quantity of heat Q' taken in by K'. These two transformations, which are of the same kind, can however be so broken up and re-arranged as to appear in the light of transformations of different kinds. For if we simply hold fast to the main fact, that the one body K has lost the quantity of heat Q, and the other K' gained the quantity Q', then the heat equivalent to the smaller of these two quantities may be considered as having been transferred directly from K to K', and it is only the difference between the two which remains to be considered as a transformation of work into heat or vice versâ. For example, let the temperature T be higher than T'; then the transference of heat on the above view is from a hotter to a colder body, and is therefore positive. Accordingly the other transformation must be negative, *i.e.* a transformation from heat into work: whence it follows that the quantity of heat Q given off by K is greater than the quantity Q' taken in by K'. Thus if we divide Q into its two component parts Q' and $Q - Q'$, then the first of these will have passed over from K to K', and the second is the quantity of heat transformed into work.

On this view the two processes appear as combined into a single process of the same kind; for the circumstance that the heat transformed into work is not derived from a third body, but from one or other of the same two bodies, between which the transference of heat takes place, makes no essential difference in the result. The temperature of the heat transformed into work is optional, and can therefore have the same value as the temperature of one of the two bodies; in which case the third body is no longer required. Accordingly for the two quantities of heat Q' and $\overline{Q-Q'}$ there must be an equation of the same form as (2), namely:

$$-\overline{Q-Q'}\times f(T)+Q'\times F(T,\,T')=0.$$

Eliminating Q by means of equation (4) and then striking out Q', we obtain

$$F(TT')=f(T')-f(T) \quad\text{..................(5).}$$

As the temperatures T and T' are any whatever, the function of two temperatures $F(TT')$, which holds for the second kind of transformation, is thus shewn to agree with the function of one temperature $f(T)$, which holds for the first kind.

For the latter function we will for brevity use a simpler symbol. For this it is convenient, for a reason which will be apparent later on, to express by the new symbol not the function itself, but its reciprocal. We will therefore put

$$\tau=\frac{1}{f(T)} \text{ or } f(T)=\frac{1}{\tau} \quad\text{..................(6),}$$

so that τ is now the unknown function of temperature which enters into the Equivalence-value. If special values of this function have to be written down, corresponding to temperatures T_1, T_2, etc., or T', T'', etc., then this can be done by simply using the indices or accents for τ itself. Thus equation (5) will become

$$F(T,\,T')=\frac{1}{\tau'}-\frac{1}{\tau}.$$

Hence the second Main Principle of the Mechanical Theory of Heat, which in this form may perhaps be called the principle of the Equivalence of Transformations, can be expressed in the following terms:

"If we call two transformations which may cancel each other without requiring any other permanent change to take place, Equivalent Transformations, then the generation out of work of the quantity of heat Q of temperature τ has the equivalence-value $\frac{Q}{\tau}$; and the transference of the quantity of heat Q from temperature T_1 to temperature T_2 has the Equivalence-value

$$Q\left(\frac{1}{\tau_2}-\frac{1}{\tau_1}\right);$$

in which τ is a function of temperature independent of the kind of process by which the transformation is accomplished."

§ 5. *Combined value of all the transformations which take place in a single Cyclical Process.*

If we write the last expression of the foregoing section in the form $\frac{Q}{\tau_2}-\frac{Q}{\tau_1}$, we see that the passage of the quantity of heat Q from temperature T_1 to T_2 has the same equivalence-value as a double transformation of the first kind, viz. the transformation of the quantity Q from heat of temperature T_1 into work, and again out of work into heat of temperature T_2. The examination of the question how far this external agreement has its actual foundation in the nature of the process would here be out of place; but in any case we may, in the mathematical determination of the Equivalence-Value, treat every transference of heat, in whatever way it may have taken place, as a combination of two opposite transformations of the first kind.

By this rule it is easy for any Cyclical Process however complicated, in which any number of transformations of both kinds take place, to deduce the mathematical expression which represents the combined value of all these transformations. For this purpose, when a quantity of heat is given off by a heat reservoir, we have no need first to enquire what portion of it is transformed into work, and what becomes of the remainder; but may instead reckon every quantity of heat given off by the heat reservoirs which occur in the cyclical process as being wholly transformed into work, and every quantity of heat taken in as being generated out of work. Thus if we assume that the bodies K_1, K_2, K_3, etc. of temperatures T_1, T_2, T_3, etc. occur as heat reservoirs, and if Q_1, Q_2, Q_3, etc. are the quantities of heat given off during the Cyclical Process (in which we will now consider quantities of heat taken in as negative quantities of heat given out*), then the combined value of all the transformations, which we may call N, will be represented as follows:

$$N = -\frac{Q_1}{\tau_1} - \frac{Q_2}{\tau_2} - \frac{Q_3}{\tau_3} - \text{etc.},$$

or using the sign of summation,

$$N = -\Sigma \frac{Q}{\tau} \qquad \text{(7)}.$$

It is here supposed that the temperatures of the bodies K_1, K_2, K_3, etc. are constant, or at least so nearly so that their variations may be neglected. If however the temperature of any one of the bodies varies so much, either through the taking in of the quantity of heat Q itself, or through any other cause, that this variation must be taken into account, then we must, for every element of heat dQ which is taken in, use the temperature which the body has at the moment of its being taken in. This naturally leads to an integration. If for the sake of generality we assume this to hold for all the bodies, then the foregoing equation takes the following form:

$$N = -\int \frac{dQ}{\tau} \qquad \text{(8)},$$

in which the integral is to be taken for all the quantities of heat given off by the different bodies.

§ 6. *Proof that in a reversible Cyclical Process the total value of all the transformations must be equal to nothing.*

If the Cyclical Process under consideration is reversible, then, however complicated it may be, it can be proved that the transformations which occur in it must cancel each other, so that their algebraical sum is equal to nothing.

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* This choice of positive and negative signs for the quantities of heat agrees with that which we made in the last chapter, where we considered a quantity of heat taken in by the variable body as positive, and a quantity given out by it as negative; for a quantity given out by a heat reservoir is taken in by the variable body, and vice versa.

For let us suppose that this is not the case, i.e. that this algebraical sum has some other value; then let us imagine the following process applied. Let all the transformations which take place be divided into two parts, of which the first has its algebraical sum equal to nothing, and the second is made up of transformations all having the same sign. Let the transformations of the first division be separated out into pairs, each composed of two transformations of equal magnitude but opposite signs. If all the heat reservoirs are of constant temperature, so that in the Cyclical Process there is only a finite number of definite temperatures, then the number of pairs which have to be formed will be also finite; but should the temperatures of the heat reservoirs vary continuously, so that the number of temperatures is indefinitely great, and therefore the quantities of heat given off and taken in must be distributed in indefinitely small elements, then the number of pairs which have to be formed will be indefinitely large. This however, by our principle, makes no difference. The two transformations of each pair are now capable of being done backwards by one or two Cyclical Processes of the form described in § 2.

Thus in the first place let the two given transformations be of different kinds, e.g. let the quantity of heat Q of temperature T be transformed into work, and the quantity of heat Q_1 be transferred from a body K_1 of temperature T_1 to a body K_2 of temperature T_2. The symbols Q and Q_1 are here supposed to represent the absolute values of the quantities. Let it be also assumed that the magnitudes of the two quantities stand in such relation to each other that the following equation, corresponding to equation (2), will hold, viz.

into work

$$-\frac{Q}{T}+Q_1\left(\frac{1}{T_2}-\frac{1}{T_1}\right)=0.$$

Then let us suppose the Cyclical Process to be performed in the reverse order, whereby the quantity of heat Q, of temperature T, is generated out of work, and another quantity of heat is transferred from the body K_2 to the body K_1. This latter quantity must then be exactly equal to the quantity Q_1, given in the above equation, and the given transformations have thus been performed backwards.

Again let there be one transformation from work into heat and one from heat into work, e.g. let the quantity of heat Q of temperature T be generated out of work, and the quantity of heat Q' of temperature T' be transformed into work, and let these two stand in such relation to each other that we may put

$$\frac{Q}{T} - \frac{Q'}{T'} = 0.$$

Then let us suppose in the first place that the same process as last described has been performed, whereby the quantity of heat Q of temperature T has been transformed into work, and another quantity Q_1 has been transferred from a body K_1 to another body K_2. Next let us suppose a second process performed in the reverse direction, in which the last-named quantity Q_1 is transferred back again from K_2 to K_1, and a quantity of heat of temperature T' is at the same time generated out of work. This transformation from work into heat must, independently of sign, be equivalent to the former transformation from heat into work, since they are both equivalent to one and the same transference of heat. The quantity of heat of temperature T', generated out of work, must therefore be exactly as great as the quantity Q' found in the above equation, and the given transformations have thus been made backwards.

Finally, let there be two transferences of heat, e.g. the quantity of heat Q transferred from a body K_1 of temperature T_1 to a body K_2 of temperature T_2, and the quantity Q'_1, from a body K'_2 of temperature T'_2 to a body K'_1 of temperature T'_1, and let these be so related that we may put

$$Q_1\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + Q'_1\left(\frac{1}{T'_1} - \frac{1}{T'_2}\right) = 0.$$

Then let us suppose two Cyclical Processes performed, in one of which the quantity Q_1 is transferred from K_2 to K_1, and the quantity Q of temperature T thereby generated out of work, whilst in the second the same quantity Q is again transformed into work, and thereby another quantity of heat transferred from K'_1 to K'_2. This second quantity must then be exactly equal to the given quantity Q'_1, and the two given transferences of heat have thus been done backwards.

When by operations of this kind all the transformations of the first division have been done backwards, there then remain the transformations, all of the like sign, of the second division, and no others whatever. Now first, if these transformations are negative then they can only be transformations from heat into work and transferences from a lower to a higher temperature; and of these the transformations of the first kind may be replaced by transformations of the second kind. For if a quantity of heat Q of temperature T is transformed into work, then we have only to perform in reverse order the cyclical process described in § 2, in which the quantity of heat Q of temperature T is generated out of work, and at the same time another quantity Q_1 is transferred from a body K_2 of temperature T_2 to another body K_1 of the higher temperature T_1. Thereby the given transformation from heat into work is done backwards, and replaced by the transference of heat from K_2 to K_1. By the application of this method, we shall at last have nothing left except transferences of heat from a lower to a higher temperature which are not compensated in any way. As this contradicts our fundamental principle, the supposition that the transformations of the second division are negative must be incorrect.

Secondly, if these transformations were positive, then since the cyclical process under consideration is reversible, the whole process might be performed in reverse order; in which case all the transformations which occur in it would take the opposite sign, and every transformation of the second division would become negative. We are thus brought back to the case already considered, which has been found to contradict the fundamental principle.

As then the transformations of the second division can neither be positive nor negative they cannot exist at all; and the first division, whose algebraical sum is zero, must embrace all the transformations which occur in the cyclical process. We may therefore write $N=0$ in equation (8), and thereby we obtain as the analytical expression of the Second Main Principle of the Mechanical Theory of Heat for reversible processes the equation

$$\int\frac{dQ}{\tau}=0 \text{ ....(VII).}$$

§ 7. *On the Temperatures of the various quantities of Heat, and the Entropy of the Body.*

In the development of Equation VII. the temperatures of the quantities of heat treated of were determined by those of the heat reservoirs from which they came, or into which they passed. But let us now consider a cyclical process, which is such that a body passes through a series of changes of condition and at last returns to its original state. This variable body, if placed in connection with the heat reservoir to receive or give off heat, must have the same temperature as the reservoir; for it is only in this case that the heat can pass as readily from the reservoir to the body as in the reverse direction, and if the process is reversible it is requisite that this should be the case. This condition cannot indeed be exactly fulfilled, since between equal temperatures there can in general be no passage of heat whatever; but we may at least assume it to be so nearly fulfilled that the small remaining differences of temperature may be neglected.

In this case it is obviously the same thing whether we consider the temperature of a quantity of heat which is being transferred as being equal to that of the reservoir or of the variable body, since these are practically the same. If however we choose the latter and suppose that in forming Equation VII. every element of heat Q is taken of that temperature which the variable body possesses at the moment it is taken in, then we can now ascribe to the heat reservoirs any other temperatures we please, without thereby making any alteration in the expression $\int\frac{dQ}{\tau}$. With this assumption as to the temperatures we may consider Equation VII. as holding, without troubling ourselves as to whence the heat comes which the variable body takes in, or where that goes which it gives off, provided the process is on the whole a reversible one.

The expression $\frac{dQ}{\tau}$, if it be understood in the sense just given, is the differential of a quantity which depends on the condition of the body, and at the same time is fully determined as soon as the condition of the body at the moment is known, without our needing to know the path by which the body has arrived at that condition; for it is only in this case that the integral will always become equal to zero as often as the body after any given variations returns to its original condition. In another paper*, after introducing a further development of the equivalence of transformations, the author proposed to call this quantity, after the Greek word τροπὴ, Transformation, the Entropy of the body. The complete explanation of this name and the proof that it correctly expresses the conditions of the quantity under consideration can indeed only be given at a later period, after the development just mentioned has been treated of; but for the sake of convenience we shall use the name henceforward.

If we denote the Entropy of the body by S we may put

$$\frac{dQ}{\tau}=dS,$$

or otherwise

$$dQ=\tau dS \quad \text{..................(VIII)}.$$

§ 8. *On the Temperature Function* τ.

To determine the temperature function τ we will apply the same method as in Chapter III. § 7, p. 81, to determine the function $\Phi(T_1, T_2)$. For, as the function τ is independent of the nature of the variable body used in the cyclical process, we may, in order to determine its form, choose any body we please to be subjected to the process. We will therefore again choose a perfect gas, and, as in the above-mentioned section, suppose a simple process performed, in which the gas takes in heat only at one temperature T, and gives it out only at another T_1. The two quantities of heat which are taken in and given out in this case, and whose absolute values we may call Q and Q_1, stand by equation (8) of the last chapter, p. 83, in the following relation to each other:

$$\frac{Q}{Q_1}=\frac{T}{T_1} \quad \text{.........................(9)}.$$

On the other hand, if we apply Equation VII. to this simple cyclical process, whilst at the same time we treat the giving out of the quantity of heat Q as equivalent to the taking in of the negative quantity $-Q$, we have the following equation :

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* Pogg. *Ann.* Vol. cxxv. p. 390.

$$\frac{Q}{\tau} - \frac{Q_1}{\tau_1} = 0, \quad \text{or } \frac{Q}{Q_1} = \frac{\tau}{\tau_1} \text{ ....(10).}$$

From equations (9) and (10) we obtain

$$\frac{\tau}{\tau_1} = \frac{T}{T_1},$$

or

$$\tau = \frac{\tau_1}{T_1} T \text{ ....(11).}$$

If we now take T as being any temperature whatever and T_1 as some given temperature, we may write the last equation thus :

$$\tau = T \times \text{Const.} \text{ ....(12),}$$

and the temperature function τ is thus reduced to a constant factor.

What value we ascribe to the constant factor is indifferent, since it may be struck out of Equation VII. and thus has no influence on any calculations performed by means of the equation. We will therefore choose the simplest value, viz. unity, and write the foregoing equation

$$\tau = T \text{ ....(13).}$$

The temperature function is now nothing more than the absolute temperature itself.

Since the foregoing determination of the function τ rests on the equations deduced for the case of gases, one of the foundations on which this determination rests will be the approximate assumption made in the treatment of gases, viz. that a perfect gas, if it expand at constant temperature, absorbs only just so much heat as is required for the external work thereby performed. Should anyone on this account have any hesitation in regarding this determination as perfectly satisfactory, he may in Equations VII. and VIII. regard τ as the symbol for the temperature function as yet undetermined, and use the equations in that form. Any such hesitation would not, in the author's opinion, be justifiable, and in what follows T will always be used in the place of τ. Equations VII. and VIII. will then be written in the following forms, which have already been given under Equations V. and VI. of the last chapter, viz.

$$\int \frac{dQ}{T} = 0,$$

$$dQ = TdS.$$

CHAPTER V.

FORMATION OF THE TWO FUNDAMENTAL EQUATIONS.

§ 1. *Discussion of the Variables which determine the Condition of the Body.*

In the general treatment of the subject hitherto adopted we have succeeded in expressing the two main principles of the Mechanical Theory of Heat by two very simple equations numbered III. and VI. (pp. 31 and 90).

$$dQ = dU + dW \quad \text{..................} \quad \text{(III)},$$

$$dQ = TdS \quad \text{.......................} \quad \text{(VI)}.$$

We will now throw these equations into altered forms which make them more convenient for our further calculations.

Both equations relate to an indefinitely small alteration of condition in the body, and in the latter it is further assumed that this alteration is affected in such a way as to be reversible. For the truth of the first equation this assumption is not necessary: we will however make it, and in the following calculation will assume, as hitherto, that we have only to do with reversible variations.

We suppose the condition of the body under consideration to be determined by the values of certain magnitudes, and for the present we will assume that two such magnitudes are sufficient. The cases which occur most frequently are those in which the condition of the body is determined by its temperature and volume, or by its temperature and pressure, or lastly by its volume and pressure. We will not however tie ourselves to any particular magnitudes, but will at first assume that the condition of the body is determined by any two magnitudes which may be called x and y; and these magnitudes we shall treat as the independent variables of our calculations. In special cases we are of course always free to take one or both of these variables as representing either one or two of the above-named magnitudes, Temperature, Volume and Pressure.

If the magnitudes x and y determine the condition of the body, we can in the above equations treat the Energy U and the Entropy S as being functions of the variables. In the same way the temperature T, whenever it does not itself form one of these variables, may be considered as a function of the two variables. The magnitudes W and Q on the contrary, as remarked above, cannot be determined so simply, but must be treated in another fashion.

The differential coefficients of these magnitudes we shall denote as follows:

$$\frac{dW}{dx} = m; \quad \frac{dW}{dy} = n \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(1)},$$

$$\frac{dQ}{dx} = M; \quad \frac{dQ}{dy} = N \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}.$$

These differential coefficients are definite functions of x and y. For suppose the variable x is changed into $x + dx$ while y remains constant, and that this alteration of condition in the body is such as to be reversible, then we are dealing with a completely determinate process, and the external work done in that process must therefore be also determinate, whence it follows that the quotient $\frac{dW}{dx}$ must equally have a determinate value. The same will hold if we suppose y to change to $y + dy$ while x remains constant. If then the differential coefficients of the external work W are determinate functions of x and y it follows from Equation III. that the differential coefficients of the quantity of heat Q taken in by the body are also determinate functions of x and y.

Let us now write for dW and dQ their expressions as functions of dx and dy, neglecting those terms which are of a higher order than dx and dy. We then have,

$$dW = mdx + ndy \qquad\qquad (3),$$

$$dQ = Mdx + Ndy \qquad\qquad (4),$$

and we thus obtain two complete differential equations, which cannot be integrated so long as the variables x and y are independent of each other, since the magnitudes m, n and M, N do not fulfil the conditions of integrability, viz.

$$\frac{dm}{dy} = \frac{dn}{dx} \text{ and } \frac{dM}{dy} = \frac{dN}{dx}.$$

The magnitudes W and Q thus belong to that class which was described in the mathematical introduction, of which the peculiarity is that, although their differential coefficients are determinate functions of the two independent variables, yet they themselves cannot be expressed as such functions, and can only be determined when a further relation between the variables is given, and thereby the way in which the variations took place is known.

§ 2. *Elimination of the quantities U and S from the two Fundamental Equations.*

Let us now return to Equation III., and substitute in it for dW and dQ expressions (3) and (4); then, collecting together the terms in dx and dy, the equation becomes,

$$Mdx + Ndy = \left(\frac{dU}{dx} + m\right) dx + \left(\frac{dU}{dy} + n\right) dy.$$

As these equations must hold for all values of dx and dy, we must have,

$$M = \frac{dU}{dx} + m,$$

$$N = \frac{dU}{dy} + n.$$

Differentiating the first equation according to y, and the second according to x, we obtain,

$$\frac{dM}{dy}=\frac{d^2U}{dxdy}+\frac{dm}{dy},$$

$$\frac{dN}{dx}=\frac{d^2U}{dydx}+\frac{dn}{dx}.$$

We may apply to U the principle which holds for every function of two independent variables, viz. that if they are differentiated according to both variables, the order of differentiation is a matter of indifference. Hence we have

$$\frac{d^2U}{dxdy}=\frac{d^2U}{dydx}.$$

Subtracting one of the two above equations from the other we obtain,

$$\frac{dM}{dy}-\frac{dN}{dx}=\frac{dm}{dy}-\frac{dn}{dx}\text{..................(5).}$$

We may now treat Equation VII. in the same manner. Putting for dQ and dS their complete expressions, it becomes,

$$Mdx+Ndy=T\left(\frac{dS}{dx}dx+\frac{dS}{dy}dy\right),$$

or

$$\frac{M}{T}dx+\frac{N}{T}dy=\frac{dS}{dx}dx+\frac{dS}{dy}dy.$$

This equation divides itself, like the last, into two, viz.

$$\frac{M}{T}=\frac{dS}{dx},$$

$$\frac{N}{T}=\frac{dS}{dy}.$$

Differentiating the first of these according to y, and the second according to x, we obtain,

$$\frac{T\frac{dM}{dy}-M\frac{dT}{dy}}{T^2}=\frac{d^2S}{dxdy},$$

$$\frac{T\frac{dN}{dx}-N\frac{dT}{dx}}{T^2}=\frac{d^2S}{dydx}.$$

But as before,

$$\frac{d^2S}{dxdy}=\frac{d^2S}{dydx};$$

hence subtracting one of the above equations from the other we obtain:

$$\frac{T\frac{dM}{dy}-M\frac{dT}{dy}}{T^2}-\frac{T\frac{dN}{dx}-N\frac{dT}{dx}}{T^2}=0,$$

or

$$\frac{dM}{dy}-\frac{dN}{dx}=\frac{1}{T}\left(M\frac{dT}{dy}-N\frac{dT}{dx}\right)\text{............(6).}$$

The two equations (5) and (6) may be also written in a somewhat different form. To avoid the use of so many letters in the formula, we will replace M and N, which were introduced as abbreviations for $\frac{dQ}{dx}$ and $\frac{dQ}{dy}$, by those differential coefficients themselves. Similarly for m and n we will write $\frac{dW}{dx}$ and $\frac{dW}{dy}$. Then the right hand side of equation (5) may be written

$$\frac{d}{dy}\left(\frac{dW}{dx}\right)-\frac{d}{dx}\left(\frac{dW}{dy}\right).$$

Thus the magnitude represented by this expression is a function of x and y, which may generally be considered as known, inasmuch as the external forces acting on the body are open to direct observation, and from these the external work can be determined. The above difference, which will occur very frequently from henceforward, we shall call "The Work

Difference referred to x and y" and shall use for it a special symbol, putting

$$D_{xy} = \frac{d}{dy}\left(\frac{dW}{dx}\right) - \frac{d}{dx}\left(\frac{dW}{dy}\right) \text{ .... (7).}$$

Through these changes equations (5) and (6) are transformed into the following:

$$\frac{d}{dy}\left(\frac{dQ}{dx}\right) - \frac{d}{dx}\left(\frac{dQ}{dy}\right) = D_{xy} \text{ ....(8),}$$

$$\frac{d}{dy}\left(\frac{dQ}{dx}\right) - \frac{d}{dx}\left(\frac{dQ}{dy}\right) = \frac{1}{T}\left(\frac{dT}{dy} \times \frac{dQ}{dx} - \frac{dT}{dx} \times \frac{dQ}{dy}\right) \text{... (9).}$$

These two equations form the analytical expressions of the two fundamental principles for reversible variations, in the case in which the condition of the body is determined by two given variables. From these equations follows a third, which is so far simpler as it contains only differential coefficients of Q of the first degree, viz.

$$\frac{dT}{dy} \times \frac{dQ}{dx} - \frac{dT}{dx} \times \frac{dQ}{dy} = TD_{xy} \text{ ....(10).}$$

§ 3. *Case in which the Temperature is taken as one of the Independent Variables.*

The above three equations are very much simplified if the temperature of the body is selected as one of the independent variables. Let us for this purpose put $y = T$, so that the two independent variables are the temperature T, and the still undetermined quantity x. Then we have first,

$$\frac{dT}{dy} = 1.$$

Again, referring to the differential coefficient $\frac{dT}{dx}$, it is assumed in its formation that, while x is changed into $x + dx$, the other variable, hitherto called y, remains constant. But as T is now itself the other variable, it follows that T must remain constant in the above differential coefficient, or in other words

$$\frac{dT}{dx} = 0.$$

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Again, if we form the Work-difference referred to x and T, this will run as follows:

$$D_{xT} = \frac{d}{dT}\left(\frac{dW}{dx}\right) - \frac{d}{dx}\left(\frac{dW}{dT}\right) \quad \text{............} \quad (11).$$

Hence equations (8), (9), (10) take the following form:

$$\frac{d}{dT}\left(\frac{dQ}{dx}\right) - \frac{d}{dx}\left(\frac{dQ}{dT}\right) = D_{xT} \quad \text{..............} (12),$$

$$\frac{d}{dT}\left(\frac{dQ}{dx}\right) - \frac{d}{dx}\left(\frac{dQ}{dT}\right) = \frac{1}{T}\frac{dQ}{dx} \quad \text{..........} \quad (13),$$

$$\frac{dQ}{dx} = TD_{xT} \quad \text{...........} \quad (14).$$

If the product TD_{xT}, given in equation (14), be substituted for $\frac{dQ}{dx}$ in equation (12), and then differentiated according to T, the following very simple equation will be the result:

$$\frac{d}{dx}\left(\frac{dQ}{dT}\right) = T\frac{dD_{xT}}{dT} \quad \text{...............} \quad (15).$$

§ 4. *Particular Assumptions as to the External Forces.*

We have hitherto made no particular assumptions as to the external forces to which the body is subjected, and to which the external work done during its alterations of condition is related. We will now consider more closely a special case, which occurs frequently in practice, namely that in which the only external force which exists, or at least the only one which is of sufficient importance to be taken into consideration, is a pressure acting on the surface of the body, everywhere normal to that surface, and of uniform intensity. In this case external work can only be done during changes in the volume of the body. Let p be the pressure per unit of surface, v the volume; then the external work done, where this volume is increased to $v + dv$, is given by the equation

$$dW = pdv \quad \text{......................} \quad (16).$$

Let us now suppose the condition of the body to be given by the values of two given variables x and y. Then the pressure p and volume v must be considered as functions of x and y. We may thus write the last equation as follows:

$$dW = p\left(\frac{dv}{dx}dx + \frac{dv}{dy}dy\right),$$

whence it follows that

$$\left.\begin{aligned} \frac{dW}{dx} &= p\frac{dv}{dx} \\ \frac{dW}{dy} &= p\frac{dv}{dy} \end{aligned}\right\} \dots\dots\dots\dots\dots\dots (17).$$

Putting these values for $\frac{dW}{dx}$ and $\frac{dW}{dy}$ in equation (7), and performing the differentiations indicated, taking note also of the fact that $\frac{d^2v}{dxdy} = \frac{d^2v}{dydx}$, we obtain

$$D_{xy} = \frac{dp}{dy} \times \frac{dv}{dx} - \frac{dp}{dx} + \frac{dv}{dy} \dots\dots\dots\dots\dots (18).$$

This value of D_{xy} we have now to apply to equations (9) and (10). Let x and T be the two independent variables; then equation (18) becomes

$$D_{xT} = \frac{dp}{dT} \times \frac{dv}{dx} - \frac{dp}{dx} \times \frac{dv}{dT} \dots\dots\dots\dots\dots (19),$$

which value we have to apply to equations (12), (14) and (15). The expression given in (18) takes its simplest form, if we choose for one of the independent variables either the volume or the pressure, or if we choose both for the two independent variables. For these cases equation (18) takes, as is easily seen, the following forms,

$$D_{vy} = \frac{dp}{dy} \dots\dots\dots\dots\dots\dots\dots\dots (20),$$

$$D_{py} = -\frac{dv}{dy} \text{ .... } (21),$$

$$D_{vp} = 1 \text{ .... } (22).$$

Lastly in the cases in which either the volume or pressure is taken as one of the independent variables, we may choose the temperature for the other. We must then put T for y in equations (20) and (21), which then become

$$D_{vT} = \frac{dp}{dT} \text{ .... } (23),$$

$$D_{pT} = -\frac{dv}{dT} \text{ .... } (24).$$

§ 5. *Frequently occurring Forms of the Differential Equations.*

In the circumstances described above, where the only external force is a uniform pressure normal to the surface, it is usual to choose as the independent variables, which are to determine the condition of the body, the quantities last mentioned in the foregoing section, viz. volume and temperature, pressure and temperature, or lastly, volume and pressure. The systems of differential equations which hold for these three cases may be easily deduced from the more general systems given above; but on account of their frequent use it may be well to collect them together in this place. The first system is the one which the author has usually employed in the treatment of special cases.

If v and T are taken as the independent variables,

$$\left.\begin{aligned}
\frac{d}{dT}\left(\frac{dQ}{dv}\right) - \frac{d}{dv}\left(\frac{dQ}{dT}\right) &= \frac{dp}{dT}, \\
\frac{d}{dT}\left(\frac{dQ}{dv}\right) - \frac{d}{dv}\left(\frac{dQ}{dT}\right) &= \frac{1}{T}\,\frac{dQ}{dv}, \\
\frac{dQ}{dv} &= T\frac{dp}{dT}, \\
\frac{d}{dv}\left(\frac{dQ}{dT}\right) &= T\frac{d^2p}{dT^2}
\end{aligned}\right\} \text{ ....(25).}$$

If p and T are taken:

$$\left.\begin{aligned} \frac{d}{dT}\left(\frac{dQ}{dp}\right)-\frac{d}{dp}\left(\frac{dQ}{dT}\right)&=-\frac{dv}{dT}, \\ \frac{d}{dT}\frac{dQ}{dp}-\frac{d}{dp}\left(\frac{dQ}{dT}\right)&=\frac{1}{T}\frac{dQ}{dp}, \\ \frac{dQ}{dp}&=-T\frac{dv}{dT}, \\ \frac{d}{dp}\left(\frac{dQ}{dT}\right)&=-T\frac{d^2v}{dT^2} \end{aligned}\right\}\quad\text{........(26).}$$

If v and p are taken:

$$\left.\begin{aligned} &\frac{d}{dp}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{dp}\right)=1, \\ &\frac{d}{dp}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{dp}\right)=\frac{1}{T}\left(\frac{dT}{dp}\times\frac{dQ}{dv}-\frac{dT}{dv}\times\frac{dQ}{dp}\right), \\ &\frac{dT}{dp}\times\frac{dQ}{dv}-\frac{dT}{dv}\times\frac{dQ}{dp}=T \end{aligned}\right\}\quad\text{.....(27).}$$

§ 6. *Equations in the case of a body which undergoes a Partial Change in its Condition of Aggregation.*

A case which permits a still further simplification peculiar to itself, and which is of special interest from its frequent occurrence, is that in which the changes of condition in the body are connected with a partial change in its Condition of Aggregation.

Suppose a body to be given, of which one part is in one particular state of aggregation, and the remainder in another. As an example we may conceive one part of the body to be in the condition of liquid and the remainder in the condition of vapour, and vapour of the particular density which it assumes when in contact with liquid: the equations deduced will however hold equally if one part of the body is in the solid condition and the other in the liquid, or one part in the solid and the other in the vaporous condition. We shall, for the sake of generality, not attempt to define more nearly the two conditions of aggregation which we are treating of, but merely call them the first and the second conditions.

Let a certain quantity of this substance be inclosed in a vessel of given volume, and let one part have the first, and the other the second condition of aggregation. If the specific volumes (or volumes per unit of weight), which the substance assumes at a given temperature in the two different conditions of aggregation, are different, then in a given space the two parts which are in the different conditions of aggregation cannot be any we please, but can only have determinate values. For if the part which exists in the condition of greater specific volume increases in size, then the pressure is thereby increased which the inclosed substance exerts on the inclosing walls, and consequently the reaction which those walls exert upon it, and finally a point will be reached, where this pressure is so great that it prevents any further passage of the substance into this condition of aggregation. When this point is reached, then, so long as the temperature of the mass and its volume, i.e. the content of the vessel, remain constant, the magnitude of the parts which are in the two conditions of aggregation can undergo no further change. If, however, whilst the temperature remains constant, the content of the vessel increases, then the part which is in the condition of aggregation of greater specific volume can again increase at the cost of the other, but only until the same pressure as before is attained and any further passage from one condition to the other thereby prevented.

Hence arises the peculiarity, which distinguishes this case from all others. For suppose we choose the temperature and the volume of the mass as the two independent variables which are to determine its condition; then the pressure is not a function of both these variables, but of the temperature alone. The same holds, if instead of the volume we take as the second independent variable some other quantity which can vary independently of the temperature, and which in conjunction with the temperature determines fully the condition of the body. The pressure must then be independent of this latter variable. The two quantities, temperature and pressure, cannot in this case be chosen as the two variables which are to serve for the determination of the body's condition.

We will now take, in addition to the temperature T, any other magnitude x, as yet left undetermined, for the second independent variable which is to determine the body's condition. Let us then consider the expression given in equation (19) for the work-difference referred to xT, viz.

$$D_{xT} = \frac{dp}{dT} \times \frac{dv}{dx} - \frac{dp}{dx} \times \frac{dv}{dT}.$$

In this we must, by what has been said, put $\frac{dp}{dx} = 0$, and we thus obtain

$$D_{xT} = \frac{dp}{dT} \times \frac{dv}{dx} \quad \text{..................(28).}$$

The three equations (12), (13), (14) are thereby changed into the following:

$$\frac{d}{dT}\left(\frac{dQ}{dx}\right) - \frac{d}{dx}\left(\frac{dQ}{dT}\right) = \frac{dp}{dT} \times \frac{dv}{dx} \quad \text{........(29),}$$

$$\frac{d}{dT}\left(\frac{dQ}{dx}\right) - \frac{d}{dx}\left(\frac{dQ}{dT}\right) = \frac{1}{T} \times \frac{dQ}{dx} \quad \text{........(30),}$$

$$\frac{dQ}{dx} = T\frac{dp}{dT} \times \frac{dv}{dx} \quad \text{..................(31).}$$

§ 7. *Clapeyron's Equation and Carnot's Function.*

To conclude the developments of the Fundamental Equations which have formed the subject of the present chapter, we may consider the equation which Clapeyron[*] deduced as a fundamental equation from the theory of Carnot, in order to see in what relation it stands to the equations we have here developed. As however Clapeyron's equation contains an unknown function of temperature, usually designated as Carnot's function, it will be advisable beforehand to throw our equations, so far as they will come under consideration, into the form which they take, if the temperature function τ, introduced in the last chapter, is treated as still indeterminate, and is not, in accordance with the value there determined, put equal to the absolute temperature T. We shall thereby obtain the advantage of fixing the relation between our temperature-function τ and Carnot's Function.

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[*] *Journal de l'Ecole Polytechnique*, Vol. xiv. (1834).

If instead of equation

$$dQ = TdS,$$

we use the less determinate Equation VIII. of the last chapter,

$$dQ = \tau dS,$$

and eliminate S from this equation, in the same manner as in § 2, we obtain instead of equation (9) the following:

$$\frac{d}{dy}\left(\frac{dQ}{dx}\right) - \frac{d}{dx}\left(\frac{dQ}{dy}\right) = \frac{1}{\tau}\left(\frac{d\tau}{dy} \times \frac{dQ}{dx} - \frac{d\tau}{dx} \times \frac{dQ}{dy}\right) \ldots (32).$$

Combining this with (8) we obtain instead of equation (16),

$$\frac{d\tau}{dy} \times \frac{dQ}{dx} - \frac{d\tau}{dx} \times \frac{dQ}{dy} = \tau D_{xy} \ldots\ldots\ldots\ldots\ldots (33).$$

If we now assume that the only external force is a uniform and normal pressure on the surface, we may use for D_{xy} the expression given in equation (18), and the above equation becomes

$$\frac{d\tau}{dy} \times \frac{dQ}{dx} - \frac{d\tau}{dx} \times \frac{dQ}{dy} = \tau\left(\frac{dp}{dy} \times \frac{dv}{dx} - \frac{dp}{dx} \times \frac{dv}{dy}\right) \ldots\ldots (34).$$

If further we choose as independent variables v and p, putting $x = v$, and $y = p$, we obtain

$$\frac{d\tau}{dp} \times \frac{dQ}{dv} - \frac{d\tau}{dv} \times \frac{dQ}{dp} = \tau \ldots\ldots\ldots\ldots\ldots (35).$$

But as τ is only a function of T, we may put

$$\frac{d\tau}{dv} = \frac{d\tau}{dT} \times \frac{dT}{dv} \text{ and } \frac{d\tau}{dp} = \frac{d\tau}{dT} \times \frac{dT}{dp}.$$

Introducing these values of $\frac{d\tau}{dv}$ and $\frac{d\tau}{dp}$ in the above equation, and dividing by $\frac{d\tau}{dT}$, we obtain, instead of the last of equations (27), the following:

$$\frac{dT}{dp} \times \frac{dQ}{dv} - \frac{dT}{dv} \times \frac{dQ}{dp} = \frac{\tau}{\frac{d\tau}{dT}} \ldots\ldots\ldots\ldots\ldots (36).$$

It is here assumed that the heat is measured in mechanical units. To introduce the ordinary measure of heat, we must divide the expression on the right-hand side by the mechanical equivalent of heat, which gives:

$$\frac{dT}{dp} \times \frac{dQ}{dv} - \frac{dT}{dv} \times \frac{dQ}{dp} = \frac{\tau}{E\frac{d\tau}{dT}} \ldots\ldots\ldots\ldots\ldots (37).$$

Clapeyron's equation agrees in form with this, since it is written*

$$\frac{dT}{dp} \times \frac{dQ}{dv} - \frac{dT}{dv} \times \frac{dQ}{dp} = C \ldots\ldots\ldots\ldots\ldots\ldots (38),$$

where C is an undetermined function of temperature, and is the same as Carnot's Function already mentioned.

If we equate the right-hand expressions of (37) and (38), we obtain the relation between C and τ, as follows:

$$C = \frac{\tau}{E\frac{d\tau}{dT}} = \frac{1}{E\frac{d(\log\tau)}{dT}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (39),$$

If, adhering to the determination of τ given by the author, we assume it to be nothing more than the absolute temperature T, then C takes the simpler form,

$$C = \frac{T}{E} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (40).$$

As equation (33) is formed by the combination of two equations, which express the first and second Main Principles, it

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* Pogg. *Ann.* Vol. LIX. p. 574.

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follows that Clapeyron's equation must be considered not as an expression of the second Main Principle in the form assumed by the author, but as the expression of a principle, which may be deduced from the combination of the first and second principles. As concerns the manner in which Clapeyron has treated his differential equation, this differs widely from the method adopted by the author. Like Carnot, he started from the assumption that the quantity of heat which must be imparted to a body during its passage from one condition to another, may be fully ascertained from its initial and final conditions, without its being necessary to know in what way and by what path the passage has taken place. Accordingly he considered Q as a function of p and v, and deduced by integrating his differential equation the following expression for Q:

$$Q = F(T) - C\phi(p, v) \quad \text{..................(41)},$$

in which $F(T)$ is any function whatever of the temperature; and $\phi(p, v)$ is a function of p and v which satisfies the following more simple differential equation:

$$\frac{dT}{dv} \times \frac{d\phi}{dp} - \frac{dT}{dp} + \frac{d\phi}{dv} = 1 \quad \text{..................(42)}.$$

To integrate this last equation we must be able to express the temperature T for the body in question as a function of p and v. If we assume that the body in question is a perfect gas, we have

$$T = \frac{pv}{R} \quad \text{..............................(43)},$$

whence

$$\frac{dT}{dv} = \frac{p}{R} \text{ and } \frac{dT}{dp} = \frac{v}{R}.$$

Hence equation (42) becomes

$$p\frac{d\phi}{dp} - v\frac{d\phi}{dv} = R \quad \text{....................(44)}.$$

Integrating, we have

$$\phi(p, v) = R \log p + \Phi(pv),$$

where $\Phi(pv)$ is any function whatever of the product pv. For this we may by equation (43) substitute any function whatever of the temperature, so that the equation becomes,

$$\phi(pv) = R \log p + \psi(T) \ldots\ldots\ldots\ldots\ldots (45).$$

If we introduce this expression for $\phi(p, v)$ in (41), and put

$$F(T) - C\psi(T) = RB,$$

where B again expresses any function whatever of the temperature, we obtain,

$$Q = R(B - C \log p) \ldots\ldots\ldots\ldots\ldots\ldots (46).$$

This is the equation which Clapeyron has deduced for the case of gases.

CHAPTER VI.

APPLICATION OF THE MECHANICAL THEORY OF HEAT TO SATURATED VAPOUR.

§ 1. *Fundamental equations for saturated vapour.*

Among the equations of the last chapter, those deduced in § 6, which refer to a partial change in the body's state of aggregation, may conveniently be treated first; inasmuch as the circumstance there mentioned, viz. that the pressure is only a function of the temperature, greatly facilitates the treatment of the subject. We will in the first place consider the passage from the liquid to the vaporous condition.

Let a weight M of any given substance be inclosed in an expansible envelope: of this let the part m be in the condition of vapour, and that vapour (as necessarily follows from its contact with the liquid) at its maximum density; and let the remainder $M-m$ be liquid. If the temperature T of the mass is given, the condition of the vaporous part, and at the same time that of the liquid part, is thereby determined. If m be also given and thereby the magnitudes of both parts known, then we know the condition of the whole mass. We will accordingly choose T and m as the independent variables, and will substitute m for x in equations (29), (30), (31) of the last chapter. Then these equations become

$$\frac{d}{dT}\left(\frac{dQ}{dm}\right)-\frac{d}{dm}\left(\frac{dQ}{dT}\right)=\frac{dp}{dT}\times\frac{dv}{dm} \quad\text{..................(1)},$$

$$\frac{d}{dT}\left(\frac{dQ}{dm}\right)-\frac{d}{dm}\left(\frac{dQ}{dT}\right)=\frac{1}{T}\times\frac{dQ}{dm} \quad\text{..................(2)},$$

$$\frac{dQ}{dm}=T\frac{dp}{dT}\times\frac{dv}{dm} \quad\text{..........................(3)}.$$

We may now denote the specific volume (i.e. the volume of a unit of weight) of the saturated vapour by s, and the specific volume of the liquid by σ. Both these magnitudes bear some relation to the temperature T and its corresponding pressure, and are therefore, like the pressure, functions of the temperature alone. If we further denote by v the total volume of the mass, we may then put

$$v = ms + (M - m)\,\sigma,$$
$$= m\,(s - \sigma) + M\sigma.$$

We will substitute for the difference $(s - \sigma)$, a simpler expression, by putting

$$u = s - \sigma \qquad \text{(4)},$$

whence it follows that

$$v = mu + M\sigma \qquad \text{(5)};$$

whence

$$\frac{dv}{dm} = u \qquad \text{(6)}.$$

The quantity of heat which must be applied to the mass, if a unit of weight of the substance, at temperature T and under the corresponding pressure, is to pass from the liquid into the vaporous condition, and which may be shortly called the vaporizing heat, may be denoted by ρ; then we have

$$\frac{dQ}{dm} = \rho \qquad \text{(7)}.$$

We will further introduce into the equations the specific heat of the substance in the liquid and vaporous condition. The specific heat here treated of is not however that at constant volume, nor yet that at constant pressure, but belongs to the case in which the pressure increases with the temperature in the same manner as the maximum expansive power of the saturated vapour. This increase of pressure has very little influence on the specific heat of the liquid, since liquids are but slightly compressible by such pressures as are herein considered. We shall hereafter explain how this influence may be calculated, in our researches on the different kinds of specific heat, and a single example will suffice here. For water at boiling-point the difference between the specific heat here considered and the specific heat at constant pressure, is only $\frac{1}{3900}$ of the latter, a difference which may be neglected. Accordingly, we may for the purposes of calculation take the specific heat of the liquid here considered as being equal to the specific heat at constant pressure, although their meaning is different. We will call this specific heat C.

With vapour it is otherwise. The specific heat here considered refers, as shewn above, to that quantity of heat which saturated vapour requires to heat it through 1°; if it is at the same time so powerfully compressed that even at the higher temperature it again returns to the saturated condition. As this compression is very considerable, this kind of specific heat is very different from all which we have hitherto treated of. We shall call it the Specific Heat of Saturated Steam, and shall denote it by H.

Bringing in the two symbols C and H, we may now at once write down the quantity of heat which is necessary to give the increase of temperature dT to the quantity of vapour m, and the quantity of liquid $M-m$. The result will be as follows:

$$mHdT + (M-m)\,CdT,$$

whence

$$\frac{dQ}{dT} = mH + (M-m)\,C,$$

or otherwise

$$\frac{dQ}{dT} = m\,(H-C) + MC \;\ldots\ldots\ldots\ldots\ldots(8).$$

From equations (7) and (8) we have

$$\frac{d}{dT}\left(\frac{dQ}{dm}\right) = \frac{d\rho}{dT} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9),$$

$$\frac{d}{dm}\left(\frac{dQ}{dT}\right) = H - C \;\ldots\ldots\ldots\ldots\ldots(10).$$

Substituting in equations (1, 2, 3) the values given in equations (7, 9, 10) we have

$$\frac{d\rho}{dT} + C - H = u\frac{dp}{dT} \quad\text{..................}(11),$$

$$\frac{d\rho}{dT} + C - H = \frac{\rho}{T} \quad\text{......................}(12),$$

$$\rho = Tu\frac{dp}{dT} \quad\text{......................}(13).$$

These are the fundamental equations of the Mechanical Theory of Heat as relates to the generation of vapour. Equation (11) is a deduction from the first fundamental principle, (12) from the second, and (13) from both together.

If it is desired to use the ordinary and not the mechanical measures for the quantities of heat, we need only divide all the members of the foregoing equations by the mechanical equivalent of heat. In this case we will denote the two specific heats and the heat of vaporization by new symbols, putting

$$c = \frac{C}{E}; \quad h = \frac{H}{E}; \quad r = \frac{\rho}{E} \quad\text{..................}(14).$$

The equations then become

$$\frac{dr}{dT} + c - h = \frac{u}{E}\left(\frac{dp}{dT}\right) \quad\text{................}(15),$$

$$\frac{dr}{dT} + c - h = \frac{r}{T} \quad\text{.......................}(16),$$

$$r = \frac{Tu}{E} \times \frac{dp}{dT} \quad\text{........................}(17).$$

§ 2. *Specific Heat of Saturated Steam.*

As the foregoing equations (15), (16) and (17), of which however only two are independent, have thus been obtained by means of the Mechanical Theory of Heat, we may make use of them in order to determine more closely two magnitudes, of which one was previously quite unknown and the other only known imperfectly; viz. the magnitude h and the magnitude s contained in u.

If we first apply ourselves to the magnitude h, or the Specific Heat of Saturated Steam, it may be worth while in the first place to give some account of the views formerly promulgated concerning this magnitude.

The magnitude h is of special importance in the theory of the steam engine, and in fact the first who published any distinct views upon it was the celebrated improver of the steam engine, James Watt. In his treatment of the subject he naturally started from those views which were based on the older theory of heat. To this class belongs especially the idea mentioned in Chapter I., viz. that the so-called total heat, i.e. the total quantity of heat taken in by a body during its passage from a given initial condition to its present condition, depends only on the present condition and not on the way in which the body has been brought into it; and that it accordingly may be expressed as a function of those variables on which the condition of the body depends. According to this view we must in our case, in which the condition of the body composed of liquid and vapour is determined by the quantities T and m, consider this quantity of heat Q as a function of T and m; accordingly we have the equation

$$\frac{d}{dT}\left(\frac{dQ}{dm}\right)-\frac{d}{dm}\left(\frac{dQ}{dT}\right)=0.$$

If we here substitute for the two second differentials their values given in equations (9) and (10), we have

$$\frac{d\rho}{dT}+C-H=0,$$

or dividing by E

$$\frac{dr}{dT}+c-h=0,$$

whence we have, to determine h, the equation,

$$h=\frac{dr}{dT}+c\;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(18).$$

This was in fact the equation which was formerly used to determine h, though not quite in the same form. To calculate h from this equation we must know the differential coefficient $\frac{dr}{dT}$, or the change of the vaporizing heat for a given change of temperature.

Watt had made experiments on the vaporizing heat of water at different temperatures, and was thereby led to a result, which may be expressed by a very simple law, commonly called Watt's law. This in its shortest form is as follows: "The sum of the free and latent heat is always constant." By this is meant that the sum of the two quantities of heat, which must be imparted to a unit of weight of water, in order to raise it from freezing point to temperature T, and then at that temperature convert it into steam, is independent of the temperature T itself. The quantity of heat required for heating the water is expressed by the integral

$$\int_a^T c\,dT,$$

in which a is the absolute temperature of freezing point. The heat of vaporization is represented by r. Watt's law therefore leads to the equation

$$r + \int_a^T c\,dT = \text{Constant} \quad\text{..................(19).}$$

Differentiating,

$$\frac{dr}{dT} + c = 0 \quad\text{........................(20),}$$

combining this with equation (18) we have

$$h = 0 \quad\text{..............................(21).}$$

This result was long considered as correct, and was expressed by the following principle: If steam of maximum density changes its volume within a vessel impermeable to heat, it always preserves its maximum density.

More recently Regnault made very careful experiments on the changes in the heat of vaporization with changes in the temperature*; and thereby discovered that Watt's law, according to which the sum of the free and latent heat is always constant, does not agree with the facts, but that this sum has an increasing value as the temperature rises. The result of his experiments is expressed in the following equation, in which instead of the absolute temperature T we introduce the temperature t reckoned from the freezing point:

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* *Relations de Experiences*, t. I.; *Mem. de l'Acad.*, t. XXI., 1847.

$$r + \int_0^t c\,dt = 606{\cdot}5 + 0{\cdot}305\,t \quad\text{..............(22).}$$

Differentiating this equation with regard to t, and then substituting $\frac{dr}{dT}$ for $\frac{dr}{dt}$, both having the same value, we have

$$\frac{dr}{dT} + c = 0{\cdot}305 \quad\text{....................(23).}$$

Combining this equation with (18) we have

$$h = {\cdot}305 \quad\text{..........................(24).}$$

This was the value of h, which it was supposed, after the publication of Regnault's experiments, must be substituted for the value zero and applied to the theory of the steam engine. Hence arose the idea that if saturated steam be compressed, and thereby heated, in such a way that it always has exactly the temperature for which the density is a maximum, it must take in heat from without; and conversely in expanding, in order to cool itself in a manner corresponding to the expansion, it must give out heat from itself. Hence we must further conclude that if saturated steam be compressed in a vessel impermeable to heat, a fall of temperature must take place; whilst in expanding the steam will not remain at its maximum density, inasmuch as its temperature cannot fall so low as this will necessitate.

Having thus explained the conclusions previously drawn in relation to h, we will now see what may be concluded from the equations here developed.

The quantity h occurs in the two equations (15) and (16); but the first of these also contains the quantity u, which cannot at present be considered as accurately known; it is therefore less convenient for determining h than the latter, which in addition to h contains only such quantities as the experiments of Regnault have determined with great accuracy in the case of water, and of many other fluids. This equation may be written

$$h = \frac{dr}{dT} + c - \frac{r}{T} \quad\text{....................(25).}$$

We have thus obtained by the Mechanical Theory of Heat a new equation for determining h, which differs from the equation (18), previously assumed to be correct, by the negative quantity $-\frac{r}{T}$, the value of which quantity is thus of great importance.

§ 3. *Numerical Value of* h *for Steam.*

If we apply equation (25) to the case of water, we must first, following Regnault, give to the sum of the first two symbols on the right-hand side the value 0·305. To determine the last symbol we must know the value of r, as a function of the temperature. Equation (22) gives us

$$r = 606{\cdot}5 + 0{\cdot}305t - \int_0^t c\,dt \;\ldots\ldots\ldots\ldots\; (26).$$

The specific heat of water c is determined according to Regnault by the following formulæ:

$$c = 1 + 0{\cdot}00004t + 0{\cdot}0000009t^2 \;\ldots\ldots\ldots\; (27).$$

Applying this, equation (26) becomes

$$r = 606{\cdot}5 - 0{\cdot}695t - 0{\cdot}0000t^2 - 0{\cdot}0000003t^3 \ldots (28).$$

Substituting this value for r in (25), and replacing T by $273 + t$, we obtain for steam the following equation:

$$h = 0{\cdot}305 - \frac{606{\cdot}5 - 0{\cdot}695t - 0{\cdot}00002t^2 - 0{\cdot}0000003t^3}{273 + t} \ldots (29).$$

The expression for r given in (28) is inconvenient from its length, and the experiments on the heat of vaporization at different temperatures, valuable as they are, can scarcely possess such a degree of accuracy as to make so long a formula necessary to represent them. Accordingly in his paper on the theory of the steam engine the author preferred to use the following formula:

$$r = 607 - 0{\cdot}708t \;\ldots\ldots\ldots\ldots\ldots\ldots\; (30).$$

The manner in which the two constants in the formula are determined will be more closely examined further on, in describing the steam engine. Here we will only give a comparison of some values determined by both formulæ, in order to shew that the difference between them is so small, that one may be substituted for the other without danger:

t	0^0	50^0	100^0	150^0	200^0
r by equation (28) ...	606·5	571·6	536·5	500·7	464·3
r by equation (30) ...	607·0	571·6	536·2	500·8	465·4

Substituting in equation (25) the expression for r in (30) we have instead of equation (29) the following:

$$h = 0{\cdot}305 - \frac{607 - 0{\cdot}708t}{273 + t},$$

or in still simpler form,

$$h = 1{\cdot}013 - \frac{800{\cdot}3}{273 + t} \quad\dots\dots\dots\dots\dots\dots \quad (31).$$

A glance at equations (29) and (31) shews that for moderate temperatures h is a negative quantity. Equation (29) gives for certain fixed temperatures the following values, which agree very closely with those calculated by equation (31):

t	0^0	50^0	100^0	150^0	200^0
h	$-1{\cdot}916$	$-1{\cdot}465$	$-1{\cdot}133$	$-0{\cdot}879$	$-0{\cdot}676$

The circumstance that the specific heat of saturated steam has a negative value, and that of so large an amount, gives it a special character of its own. We may explain in the following manner the cause of this singular condition. If steam is compressed, heat is generated by the work thereby expended, and this heat is more than sufficient to raise the temperature of the steam to the point at which the new density is the maximum density. Accordingly if the steam is to be treated in such a way that it remains saturated, it must be deprived of a part of the heat thus generated. In like manner in the expansion of steam more heat is converted into work than is necessary to cool the steam so far only that it remains exactly in the condition of saturated steam. Accordingly if this last condition is to hold heat must be imparted during the expansion.

Should the original saturated steam be contained in a vessel impermeable to heat, it will be superheated during compression and will be in part condensed during expansion.

The conclusion that the specific heat of saturated steam is negative was drawn by Rankine and by the author independently, and about the same time*. Rankine however developed only the first of the two equations (15) and (16), which contain h, and this in a somewhat different form. The second it was impossible for him to develope, since he was without the second fundamental principle, which was necessary thereto. Since in the first equation there occurs together with h the specific volume of the saturated steam, which is contained in u, Rankine in order to determine this applied to saturated steam the law of Mariotte and Gay-Lussac, which, as we shall see further on, is inaccurate. More exact determinations of h could only be accomplished by means of equation (16), which was first established by the author.

§ 4. *Numerical Value of* h *for other Vapours.*

When equation (25) was first published, Regnault's determinations of the specific heat and heat of vaporization as functions of temperature had been performed only for the case of water†; and therefore the numerical value of h could be given for water only. Regnault has since extended his measurements to other fluids‡, and it is now possible to apply the equation to obtain the numerical value of h for these fluids. We thus obtain the following results.

Bi-sulphide of Carbon: CS_2. According to Regnault we have

$$\int_0^t c dt = 0{\cdot}23523t + 0{\cdot}0000815t^2,$$

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* Rankine's paper was read before the Royal Society of Edinburgh in February, 1850, and printed in the *Transactions*, Vol. xx. p. 147. The author's paper was read before the academy of Berlin in February, 1850, and printed in Poggendorf's *Annalen*, Vol. LXXIX. pp. 368 and 500.

† *Relations des Experiences*, Vol. I., Paris, 1847.

‡ *Relations des Experiences*, Vol. II., Paris, 1862.

$$r+\int_0^t c dt = 90+0{\cdot}14601t-0{\cdot}0004123t^2:$$

whence we have

$$c=0{\cdot}23523+0{\cdot}0001630t,$$
$$r=90{\cdot}00-0{\cdot}08922t-0{\cdot}0004938t^2.$$

Substituting these values, equation (25) becomes

$$h=0{\cdot}14601-0{\cdot}0008246t-\frac{90{\cdot}00-0{\cdot}08922t-0{\cdot}0004938t^2}{273+t},$$

hence we obtain for h the following values amongst others:

t	0^0	100^0
h	$-0{\cdot}1837$	$-0{\cdot}1406$

The specific heat of the saturated vapour of Bi-sulphide of Carbon is thus negative like that of steam, but its values are smaller.

Ether: $C_4H_{10}O$. According to Regnault we have

$$\int_0^t c dt = 0{\cdot}52900t+0{\cdot}00029587t^2,$$

$$r+\int_0^t c dt = 94{\cdot}00+0{\cdot}45000t-0{\cdot}00055556t^2,$$

whence we have

$$c=0{\cdot}529+0{\cdot}00059174t,$$
$$r=94{\cdot}00-0{\cdot}07900t-0{\cdot}0008514t^2.$$

Equation (25) thus becomes

$$h=0{\cdot}45000-0{\cdot}0011111\,t-\frac{94{\cdot}00-0{\cdot}07900t-0{\cdot}0008514t^2}{273+t},$$

and from this the following values are deduced:

t	0^0	100^0
h	$-0{\cdot}1057$	$-0{\cdot}1309$

In the case of Ether therefore the specific heat of saturated steam has, at least at ordinary temperatures, a *positive* value.

Chloroform: $CHCl_3$. According to Regnault we have

$$\int_0^t c dt = 0{\cdot}23235t + 0{\cdot}00005072t^2,$$

$$r + \int_0^t c dt = 67 + 0{\cdot}1375t;$$

whence we have

$$c = 0{\cdot}23235 + 0{\cdot}00010144t,$$

$$r = 67 - 0{\cdot}09485t - 0{\cdot}00005072t^2.$$

Equation (25) thus becomes

$$h = 0{\cdot}1375 - \frac{67 - 0{\cdot}09485t - 0{\cdot}00005072t^2}{273 + t},$$

and from this the following values are deduced:

t	0^0	100^0
h	$-0{\cdot}1079$	$-00{\cdot}153$

Bi-Chloride of Carbon: CCl_4. According to Regnault we have:

$$\int_0^t c dt = 0{\cdot}19798t + 0{\cdot}0000906t^2,$$

$$r + \int_0^t c dt = 52 + 0{\cdot}14625t - 0{\cdot}000172t^2;$$

whence we have

$$c = 0{\cdot}19798 + 0{\cdot}0001812t,$$

$$r = 52 - 0{\cdot}05173t - 0{\cdot}0002626t^2.$$

Equation (25) thus becomes

$$h = 0{\cdot}14625 - 0{\cdot}000344t - \frac{52{\cdot}00 - 0{\cdot}05173 - 0{\cdot}0002626t^2}{273 + t};$$

and from this the following values are deduced:

t	0^0	100^0
h	$-0{\cdot}0442$	$-0{\cdot}0066$

Aceton: C_3H_6O. According to Regnault we have

$$\int^t cdt = 0{\cdot}50643t + 0{\cdot}0003965t^2,$$

$$r + \int_0^t cdt = 140{\cdot}5 + 0{\cdot}36644t - 0{\cdot}000516t^2;$$

whence we have

$$c = 0{\cdot}50643 + 0{\cdot}0007930t,$$
$$r = 140{\cdot}5 - 0{\cdot}13999t - 0{\cdot}0009125t^2.$$

Equation (25) thus becomes

$$h = 0{\cdot}36644 - 0{\cdot}001032t - \frac{140{\cdot}5 - 0{\cdot}13999t - 0{\cdot}0009125t^2}{273 + t},$$

and from this the following values are deduced:

t	0^0	100^0
h	$-0{\cdot}1482$	$-0{\cdot}0515$

In addition to the above Regnault has investigated Alcohol, Benzine, and Oil of Turpentine, so far as to determine the values of $r + \int_0^t cdt$. For Alcohol and Turpentine he gives no empirical formulæ for ascertaining their values, on account of the irregularities in the experiments; and for Benzine he has not expressed $\int_0^t cdt$ as a function of temperature, but has only investigated a mean value of the Specific Heat for a narrow interval of temperature. The numerical value of h is thus much more uncertain for these fluids than for those given above, and accordingly we shall not treat of them further.

In all the formulæ for h given above we see that its value increases as the temperature rises. In the only case, that of ether, in which it is positive at ordinary temperatures, its absolute value increases as the temperature rises. In the other cases, in which it is negative, its absolute value diminishes; it thus approaches to zero, and it would appear that at some higher temperature it would attain the value zero, and at still higher temperatures would become positive. To determine the temperature at which $h = 0$, we have by equation (25)

$$\frac{dr}{dT} + c - \frac{r}{T} = 0 \quad\text{.....................(32).}$$

In this equation we must, as above, express c and r as functions of t, and then solve it with regard to t.

The empirical formulæ of Regnault, by means of which we have expressed c and r as functions of t, should not of course be applied much beyond the limits of temperature within which Regnault carried out his experiments. Hence the determination of the temperature for which $h = 0$ is in many cases impossible, as for instance with water, where the equations obtained by putting $h = 0$ in (29) and (31) would lead to a value for t of about 500°, whereas the equations are only applicable up to somewhat over 200°. But with other fluids the temperature for which $h = 0$, and above which h is positive, lies within the limits of application of the formulæ. Thus Cazin* calculates this temperature for Chloroform at 123·48°, and for Bi-chloride of Carbon at 128·9°.

§ 5. *Specific Heat of Saturated Steam, as proved by Experiment.*

The result arrived at by theory, that the Specific Heat of saturated steam is negative, and that therefore saturated steam, if expanded in a non-conducting envelope, must partially condense, has since been experimentally proved by Hirn†. A cylindrical vessel of metal was fitted at the two ends with parallel plates of glass, so that it could be seen through. This, when filled with steam at high pressure was perfectly clear; but when a cock was suddenly opened, so that part of the steam escaped, and the remainder expanded, a thick cloud appeared in the interior of the cylinder, proving a partial condensation of the steam. Subsequently, when Volume II. of Regnault's *Relation des Expériences* had appeared, containing the data, given above, to determine h for other fluids, and shewing that for ether h must be positive, Hirn proceeded to experiment with that vapour also. His description is as follows*: "To the neck of a strong crystal flask I connected a pump, the capacity of which was nearly equal to that of the flask, and which was provided with a cock at the bottom. Some ether was poured into the flask, and it was immersed to the neck in water at about 50°. The cock was then kept open, until all the air was assumed to be expelled. Then the cock was closed, and the pump plunged into the hot water with the flask: whereupon the ether vapour raised the piston to the top. The apparatus was now suddenly taken from the water, and the piston forced rapidly down. At this moment, but for a moment only, the flask became filled with a distinct cloud." It was thus shewn that ether vapour behaves conversely to steam, partially condensing, not during expansion, but during compression; a fact which is in accordance with the opposite sign of h in the two cases.

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* *Annales de Chimie et de Physique*, Series IV. Vol. XIV.

† Bulletin 133 *de la Société Industrielle de Mulhouse*, p. 137.

To check this conclusion Hirn made an exactly similar experiment with Bi-sulphide of Carbon. The result was that on forcing down the piston the flask remained perfectly transparent. This is again in accordance with the theory, since with Bi-sulphide of Carbon, as with water, h is negative, and compression of the vapour produces a rise of temperature, and not a fall. Some years later Cazin†, aided by the *Association scientifique*, made with great care and skill a similar series of experiments, in some respects more extended. He used as before a cylinder of metal, fitted with glass at the ends. This was placed in a bath of oil, so as to give it the exact temperature proper for the experiment. The first series of experiments embraced only the expansion of steam; the arrangement was such that, when the cylinder was filled with vapour, a cock could be opened, through which a part of the vapour escaped either into the atmosphere or into an air vessel, the pressure in which could be kept at any given point below the pressure of the vapour. In a second series of experiments a pump was connected with the cylinder; this was placed in the same bath of oil, and the piston could be moved rapidly backwards or forwards by special mechanism, so as to increase or diminish the volume of the vapour.

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* *Cosmos*, 10 April, 1863.

† *Annales de Chimie et de Physique*, Series IV. Vol. XIV.

By these experiments the results obtained by Hirn for steam and ether were confirmed, and with the second apparatus a double proof was given in each case, viz. both by rarefaction and condensation. Steam formed a cloud during rarefaction, whilst it remained quite clear during condensation. Ether, on the contrary, formed a cloud during condensation, and remained clear during rarefaction. Some special experiments were further made with vapour of chloroform. As mentioned above, in the case of chloroform *h*, which is negative at lower temperatures, becomes zero at a temperature which Cazin has calculated at 123·48°, and at still higher temperatures is positive. This vapour must thus partially condense during expansion at lower temperatures, and must partially condense during compression at higher temperatures beyond the point of transition. With the first apparatus, which only allowed of expansion, clouds were observed during expansion at temperatures up to 123°. At temperatures above 145° there was no formation of cloud. Between 123° and 145° the conditions were somewhat different according to the degree of expansion. With a small degree of expansion there was no cloud; with a higher degree some formation of a cloud appeared towards the end of the process. The explanation of this is simple. The high expansion had produced a considerable fall of temperature, and the vapour had thereby been reduced to the temperature at which expansion is accompanied by a fall of temperature. The result is thus completely in accordance with the theory. With the second apparatus the vapour of chloroform formed a cloud during expansion up to 130°, whilst it remained perfectly transparent during compression. Above 136° a cloud was formed during compression, whilst it remained clear during expansion. The theory is hereby more fully established than by the first apparatus. The circumstance that the temperature at which the law of the vapour changes appeared in these experiments to lie between 130° and 136°, whilst theory gives it at 123·48°, is not a matter of great importance. On the one hand these experiments are not adapted for an accurate determination of this temperature, because they always involve finite changes of volume of considerable magnitude, whereas the theory embraces indefinitely small changes only. On the other hand, Cazin himself mentions that his chloroform was not chemically pure, and required for a given vapour-pressure a higher temperature than that found by Regnault. Having regard to these circumstances, the theory must be considered as being fully confirmed by experiment.

§ 6. *Specific Volume of Saturated Vapour.*

We will now consider the second of the two quantities mentioned at the beginning of § 2, viz. s, or the specific volume of the saturated vapour.

It was formerly the custom to use the law of Mariotte and Gay-Lussac, in order to calculate the volume which a gas assumes under different conditions of temperature and pressure, and to take no account of whether the vapour was in the saturated or superheated condition. It is true that from many quarters doubts were expressed, whether vapours really followed this law up to the saturation point: but, as the experimental determination of the volumes offered great difficulties, and a theoretical determination was impossible from the want of well-established principles, it remained the custom to apply the above law in this case, so as at least to arrive at some sort of determination of the volume of saturated vapour. But the equations obtained by the author, and given at the end of § 1, now offer us a means of arriving at a strict theoretical calculation for the volume of saturated vapour, which, when the data are given, may be worked out in practice. For in these equations occurs the quantity u, which $= s - \sigma$, where σ is the specific volume of the fluid. This, as a rule, is very small in comparison with s, and may be neglected in many calculations; but it is still a known quantity, and may be taken account of without difficulty.

Substituting $(s-\sigma)$ for u in the last of these equations, (17), we obtain

$$r=\frac{T(s-\sigma)}{E}\times\frac{dp}{dT}\dots\dots\dots\dots\dots\dots(33),$$

or, solving the equation for s,

$$s=\frac{Er}{T\frac{dp}{dT}}+\sigma\dots\dots\dots\dots\dots\dots\dots\dots(34).$$

By this equation the specific volume of the saturated vapour may be calculated for all substances, whose pressure p and heat of vaporization r are known as functions of the temperature.

§ 7. *Departure from the law of Mariotte and Gay-Lussac in the case of Saturated Steam.*

We will first apply the foregoing equations to ascertain whether saturated steam follows the law of Mariotte and Gay-Lussac, or how far or in what way it departs from it.

If it follows the law the following equation must hold:

$$\frac{ps}{T}=\text{const.},$$

or, substituting $a+t$ for T, and multiplying by $\frac{a}{E}$,

$$\frac{1}{E}ps\frac{a}{a+t}=\text{const.}:$$

but from equation (33), substituting $a+t$ for T, we obtain

$$\frac{1}{E}p(s-\sigma)\frac{a}{a+t}=\frac{ar}{(a+t)^2\frac{1}{p}\frac{dp}{dt}}\dots\dots\dots\dots(35).$$

As the difference $(s-\sigma)$ differs little from s, the left-hand side of these two equations is very nearly the same, and, to ascertain how saturated steam is related to the law of Mariotte and Gay-Lussac, we have only to enquire whether the right-hand side of the last equation is constant, or varies with the temperature. To ascertain whether the successive values of an expression are equal to each other, or in what way they depart from each other, is a very simple matter; and the form of equation (35) is very well adapted for this purpose. The author has calculated the values of this expression for a series of temperatures from 0° to 200°, applying the numbers given by Regnault to r and p. For r, the heat of vaporization, the equation (28) was used, viz.:

$$r = 606{\cdot}5 - 0{\cdot}695t - 0{\cdot}00002t^2 - 0{\cdot}0000003t^3.$$

The more simple formula (30) might have been used without any great difference in the results. To obtain p, the author first applied the numbers which Regnault has published in his well-known large Tables, in which the pressure of steam for every degree from −32° to +230° is given. He found however some peculiar variations from the regular course of the numbers, which in certain ranges of temperature had quite a different character from what they had in others; and he soon discovered that the source of these variations lay in the fact that Regnault had calculated his numbers by empirical formulæ, and that for different ranges of temperature he had employed different formulæ. It then appeared desirable to the author to emancipate himself entirely from the influence of empirical formulæ, and to confine himself to those numbers which express simply the results of the observations, because these are specially adapted for comparison with theoretical results. Regnault, in order to obtain from his numerous observations the most probable values, used the aid of graphical methods. He constructed curves of which the abscissæ represent the temperature, and the ordinates the pressure p, and which run from −33° to +230°. From 100° to 230° he also constructed a curve in which the ordinates represented not p itself, but the logarithm of p. From this have been obtained the following values, which may be considered the most direct results of his observations, and from which were also taken the values which served for the calculation of his empirical formulæ.

t in Centigrade Degrees of the Air-thermometer.	p in Millimetres.	t in Centigrade Degrees of the Air-thermometer.	p in Millimetres,	
			according to the Curve of Numbers.	according to the Curve of Logarithms *.
– 20°	0·91	110°	1073·7	1073·3
– 10	2·08	120	1489·0	1490·7
0	4·60	130	2029·0	2030·5
10	9·16	140	2713·0	2711·5
20	17·39	150	3572·0	3578·5
30	31·55	160	4647·0	4651·6
40	54·91	170	5960·0	5956·7
50	91·98	180	7545·0	7537·0
60	148·79	190	9428·0	9425·4
70	233·09	200	11660·0	11679·0
80	354·64	210	14308·0	14325·0
90	525·45	220	17390·0	17390·0
100	760·00	230	20915·0	20927·0

In order to make the required calculation with these data, the values of $\frac{1}{p}\frac{dp}{dt}$ were determined from the above table for the temperatures 5°, 15°, 25°, etc., in the following manner. As $\frac{1}{p}\frac{dp}{dt}$ diminishes but slowly as the temperature increases, the decrease was taken as uniform for every interval of 10°, i.e. from 0° to 10°, from 10° to 20°, and so on; e.g. the value for 25° was taken as the mean of the two values for 20° and 30°. Then since

$$\frac{1}{p}\frac{dp}{dt} = \frac{d(\log p)}{dt},$$

the following formulæ could be used:

$$\left(\frac{1}{p}\frac{dp}{dt}\right)_{25^\circ} = \frac{\log p_{30} - \log p_{20}}{10},$$

or otherwise

$$\left(\frac{1}{p}\frac{dp}{dt}\right)_{25^\circ} = \frac{\mathrm{Log}\, p_{30} - \mathrm{Log}\, p_{20}}{10M} \ldots\ldots\ldots\ldots\ldots (36),$$

where Log signifies the common system of logarithms, and M

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* In this column are given, instead of the Logarithms given directly by the curve and used by Regnault, the numbers which correspond with them, in order to compare them with the numbers in the previous column.

the modulus of that system. By the help of these values of $\frac{1}{p}\frac{dp}{dt}$ and of the values of r given by the equation stated above, and lastly of the value 273 for a, the values were calculated which the expression on the right-hand side of equation (35) and therefore likewise the expression

$$\frac{1}{E}p(s-\sigma)\frac{a}{a+t}$$

assumes for the temperatures 5°, 15°, 25°, etc. These values are given in the second column of the table below. For temperatures over 100° the two series of numbers found above for p were both made use of, and the two results thus obtained are placed side by side. The meaning of the third and fourth columns will be more fully explained below.

1. t in Degrees Centigrade of the Air-thermometer.	$\frac{1}{E}p(s-\sigma)\frac{a}{a+t}$.			4. Differences.	
	2. According to Experiment.		3. According to Equation (38).		
5°	30·93		30·46	−0·47	
15	30·60		30·38	−0·22	
25	30·40		30·30	−0·10	
35	30·23		30·20	−0·03	
45	30·10		30·10	0·00	
55	29·98		30·00	+0·02	
65	29·88		29·88	0·00	
75	29·76		29·76	0·00	
85	29·65		29·63	−0·02	
95	29·49		29·48	−0·01	
105	29·47	29·50	29·33	−0·14	−0·17
115	29·16	29·02	29·17	+0·01	+0·15
125	28·89	28·93	28·99	+0·10	+0·06
135	28·88	29·01	28·80	−0·08	−0·21
145	28·65	28·40	28·60	−0·05	+0·20
155	28·16	28·25	28·38	+0·22	+0·13
165	28·02	28·19	28·14	+0·12	−0·05
175	27·84	27·90	27·89	+0·05	−0·01
185	27·76	27·67	27·62	−0·14	−0·05
195	27·45	27·20	27·33	−0·12	+0·13
205	26·89	26·94	27·02	+0·13	+0·08
215	26·56	26·79	26·68	+0·12	−0·11
225	26·64	26·50	26·32	−0·32	−0·18

This table at once shews that $\frac{1}{E}p(s-\sigma)\frac{a}{a+t}$ is not constant, as it must be if the law of Mariotte and Gay-Lussac holds, but decreases decidedly as the temperature rises. Between 35° and 95° this decrease appears very regular. Below 35° the decrease is less regular, the simple explanation being that here the pressure p and its differential coefficient $\frac{dp}{dt}$ are very small, and therefore small errors in their determination, which are quite within the limits of errors of observation, may yet become relatively important. Above 100° the values of the expression are not so regular as between 25° and 95°, but shew on the whole a similar rate of decrease: and if we make a graphic representation of these values, it is found that the curve, which below 100° passes exactly through the points determined by the numbers contained in the table, can be readily continued up to 230° in such a way that these points are distributed equally on both sides of it.

The course of this curve can be expressed with sufficient accuracy for the whole extent of the table by an equation of the form

$$\frac{1}{E}p\,(s-\sigma)\,\frac{a}{a+t}=m-ne^{kt}\text{............ (37)},$$

where e is the base of Napierian logarithms, and m, n, k are constants. If we determine the latter from the values which the curve gives for 45°, 125°, and 205°, we obtain

$$m=31{\cdot}549\,;\ n=1{\cdot}0486\,;\ k=0{\cdot}007138\text{......}(37a),$$

and if for convenience we use common logarithms, we finally obtain

$$\text{Log}\left[31{\cdot}549-\frac{1}{E}p\,(s-\sigma)\,\frac{a}{a+t}\right]=0{\cdot}0206+0{\cdot}003100t\text{...}(38).$$

The numbers contained in the third column of the table are calculated from this equation, and in the fourth column are given the differences between these and the numbers in the second column.

§ 8. *Differential Coefficients of* $\frac{ps}{ps_0}$.

The foregoing analysis leads easily to a formula, from which we can ascertain more exactly the mode in which steam departs from the law of Mariotte and Gay-Lussac. Assuming this law to hold, we shall be able to put

$$\frac{ps}{ps_0}=\frac{a+t}{a},$$

where ps_0 represents the value of ps at 0°. The differential coefficient $\frac{d}{dt}\left(\frac{ps}{ps_0}\right)$ would then have a constant value, viz. the well-known coefficient of expansion $\frac{1}{a}=0{\cdot}003665$. Instead of this, equation (37) gives, if we use s in place of $(s-\sigma)$, the equation

$$\frac{ps}{ps_0}=\frac{m-ne^{kt}}{m-n}\times\frac{a+t}{a} \quad\ldots\ldots\ldots\ldots\ldots (39),$$

whence

$$\frac{d}{dt}\left(\frac{ps}{ps_0}\right)=\frac{1}{a}\times\frac{m-n\,[1+k\,(a+t)]\,e^{kt}}{m-n}\ldots\ldots (40).$$

Thus the differential coefficient is not a constant, but a function which decreases as the temperature increases. This function, if we substitute for m, n, and k the numbers given in (37a), has amongst others the following values, for different temperatures.

t.	$\frac{d}{dt}\left(\frac{ps}{ps_0}\right)$.	t.	$\frac{d}{dt}\left(\frac{ps}{ps_0}\right)$.	t.	$\frac{d}{dt}\left(\frac{ps}{ps_0}\right)$.
0°	0·00342	70°	0·00307	140°	0·00244
10	0·00338	80	0·00300	150	0·00231
20	0·00334	90	0·00293	160	0·00217
30	0·00329	100	0·00285	170	0·00203
40	0·00325	110	0·00276	180	0·00187
50	0·00319	120	0·00266	190	0·00168
60	0·00314	130	0·00256	200	0·00149

From the above table we see that it is only at low temperatures that the variations from the law of Mariotte and Gay-Lussac are small, and that at higher temperatures, e.g. above 100°, they can by no means be neglected.

A glance at the table is sufficient to shew that the values found for $\frac{d}{dt}\left(\frac{ps}{ps_0}\right)$ are smaller than 0·003665; whereas it is known that for the gases which vary considerably from the law of Mariotte and Gay-Lussac, such as carbonic acid and sulphuric acid, the coefficient of expansion is not smaller, but greater than the above number. Hence this differential coefficient cannot be taken to correspond with the coefficient of expansion which relates to increase of volume by heating at constant pressure, nor yet with the figure obtained if we leave the volume constant during the heating, and then observe the increase of the expansive force. Thus we have here a third special case of the general differential coefficient $\frac{d}{dt}\left(\frac{ps}{ps_0}\right)$, viz. that in which the pressure increases during the heating under the same conditions as in the case of steam, when this retains its maximum density; and this case must be considered for carbonic acid likewise, if we are to establish a comparison.

Steam has at about 108° an expansive force equal to 1 metre of mercury, and at 129½° equal to 2 metres. We will examine what takes place with carbonic acid, if this is also heated by 21½°, and thereby the pressure increased from 1 to 2 metres. Regnault* gives as the coefficient of expansion of carbonic acid at constant pressure 0·00371 if the pressure is 760 mm., and 0·003846 if the pressure is 2520 mm. For a pressure of 1500 mm., the mean between 1 and 2 metres, the coefficient of expansion, if assumed to increase in proportion to the pressure, will have the value 0·003767. If carbonic acid under this mean pressure is heated from 0° to 21½°, the quantity $\frac{pv}{pv_0}$ will increase from 1 to

$$1 + 0{\cdot}003767 \times 21{\cdot}5 = 1{\cdot}08099.$$

Again other experiments of Regnault's† have shewn that, if carbonic acid, which had a pressure of about 1 m. at a temperature of about 0°, is loaded with a pressure of 1·98292 m., the quantity pv decreases in the ratio of $1:0·99146$; or for an increase of pressure from 1 to 2 ms., it will decrease in the ratio of $1:0·99131$. Now if both of these take place together, viz. a rise of temperature from 0° to 21½°, and a rise of pressure from 1 to 2 ms., then the quantity $\frac{pv}{pv_0}$ must increase from 1 to $1·08099 \times 0·99131 = 1·071596$ very nearly, whence we obtain as the mean value of the differential coefficient $\frac{d}{dt}\left(\frac{pv}{pv_0}\right)$,

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* *Relation des Expériences*, t. I. Mem. 1.

† *Relation des Expériences*, t. I. Mem. 6.

$$\frac{0·071596}{21·5} = 0·00333.$$

We thus see that for the case here considered we have a value for carbonic acid which is less than 0·003665, and there is therefore less ground for surprise at obtaining the same result for steam at its maximum density.

If we seek to determine on the other hand the actual coefficient of expansion for steam, or the number which shews how far a quantity of steam expands, if it is taken at a given temperature and at its maximum density and then heated, apart from water, at constant pressure, we shall certainly obtain a value which is larger, and probably much larger, than 0·003665.

§ 9. *Formula to determine the Specific Volume of Saturated Steam, and its comparison with experiment.*

From equation (37), and equally from equation (34), the relative values of $s - \sigma$, and therefore to a close approximation those of s, may be calculated for different temperatures, without needing to know the Mechanical Equivalent E. If however we wish to calculate from the equations the absolute value of s, we must either know E, or must attempt to eliminate it by the help of some other known quantity. At the time when the author first began these researches, several values of E had been given by Joule, taken from various methods of experiment: these differed widely from each other, and Joule had not announced which he considered the most probable. In this uncertainty the author determined to attempt the determination of the absolute value of s from another starting point, and he believes that his method still possesses interest enough to merit description.

The specific weight of gases and vapours is generally expressed by comparing the weight of a unit of volume of the gas or vapour with the weight of a unit of volume of atmospheric air at the same pressure and temperature. Similarly the specific volume may be expressed by comparing the volume of a unit of weight of the gas or vapour with the volume of a unit of weight of atmospheric air at the same pressure and temperature. If we apply this latter method to saturated steam, for which we have denoted the volume of a unit of weight by s, and if we designate by v' the volume of a unit of weight of atmospheric air at the same pressure and temperature, then the quantity under consideration is given by the fraction $\frac{s}{v'}$.

For s we have the following equation, obtained from (37) by neglecting σ:

$$s = \frac{E(a+t)}{ap} \times (m - ne^{kt}) \quad \text{............(41)}.$$

For v' we have by the law of Mariotte and Gay-Lussac the equation

$$v' = R' \frac{a+t}{p}.$$

These two equations give

$$\frac{s}{v'} = \frac{E}{R'a}(m - ne^{kt}) \quad \text{..................(42)}.$$

If we form the same equations for any given temperature t_0, and denote the corresponding value of $\frac{s}{v'}$ by $\left(\frac{s}{v'}\right)_0$, we obtain

$$\left(\frac{s}{v'}\right)_0 = \frac{E}{R'a}(m - ne^{kt_0}).$$

If by the help of this equation we eliminate the constant factor $\frac{E}{R'a}$ from (42), we obtain

$$\frac{s}{v'} = \left(\frac{s}{v'}\right)_0 \frac{m - ne^{kt}}{m - ne^{kt_0}} \quad \text{..............(43).}$$

The question is now whether, for any given temperature t_0, the quantity $\left(\frac{s}{v'}\right)_0$ or its reciprocal $\left(\frac{v'}{s}\right)_0$, which expresses the specific weight of the steam at temperature t_0, can be determined with sufficient certainty.

The ordinary values given for the specific weight of steam refer not to saturated but to highly superheated steam. They agree very well, as is known, with the theoretical values which may be deduced from the well-known law as to the relation between the volume of a compound gas, and those of the gases which compose it. Thus e.g. Gay-Lussac found for the specific weight of steam the experimental value 0·6235; whilst the theoretical value obtained by assuming two units of hydrogen and one unit of oxygen to form, by combining, 2 units of steam, is

$$\frac{2 \times 0{\cdot}06926 \times 1{\cdot}10563}{2} = 0{\cdot}622.$$

This value of the specific weight we cannot in general apply to saturated steam, since the table in the last section, which gives the values of $\frac{d}{dt}\left(\frac{ps}{ps_0}\right)$, indicates too large a divergence from the law of Mariotte and Gay-Lussac. On the other hand the table shews that the divergences are smaller as the temperature is lower; hence, the error will be insignificant if we assume that at freezing temperature saturated steam follows exactly the law of Mariotte and Gay-Lussac, and accordingly take 0·622 as the specific heat at that temperature. In strict accuracy we must go yet further and put the temperature, at which the specific weight of saturated steam has its theoretical value, still lower than freezing point. But, as it would be somewhat questionable to use equation (37), which is only empirical, at such low temperatures, we shall content ourselves with the above assumption. Thus giving to t_0 the value 0, and at the same time putting $\left(\frac{v'}{s}\right)_0 = 0{\cdot}622$ and therefore $\left(\frac{s}{v'}\right)_0 = \frac{1}{0{\cdot}622}$, we obtain from equation (43)

$$\frac{s}{v'} = \frac{m - ne^{kt}}{0{\cdot}622\,(m-n)} \quad \ldots\ldots\ldots\ldots\ldots\ldots(44).$$

From this equation, using the values for m, n, and k given in (37*a*), the quantity $\frac{s}{v'}$, and therefore the quantity s, may be calculated for each temperature. The foregoing equation may be thrown into a more convenient form by putting

$$\frac{s}{v'} = M - N\alpha^t \ldots\ldots\ldots\ldots\ldots\ldots\ldots(45),$$

and by giving to the constants M, N, and α the following values, calculated from those of m, n, and k:

$$M = 1{\cdot}663\,;\ N = 0{\cdot}05527;\ \alpha = 1{\cdot}007164 \ldots(45a).$$

To give some idea of the working of this formula, we give in the following table certain values of $\frac{s}{v'}$, and of its reciprocal $\frac{v'}{s}$, which for the sake of brevity we shall denote by the letter d, already used to designate specific weight.

t	0°	50°	100°	150°	200°
$\frac{s}{v'}$	1·608	1·585	1·550	1·502	1·433
d	0·622	0·631	0·645	0·666	0·698

The result that saturated steam diverges, so widely as the above formulæ and tables indicate, from the law of Mariotte and Gay-Lussac, which had been previously applied to it without reserve, met at first, as mentioned in another place, with the strongest opposition, even from very competent

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judges. The author believes however that it is now generally accepted as correct.

It has also received an experimental verification by the experiments of Fairbairn and Tate*, published in 1860. The results of their experiments are compared in the following table, on the one hand with the results previously obtained by assuming the specific weight to be 0·622 at all temperatures, and on the other hand with the values calculated by equation (45).

Temperature in Degrees Centigrade.	Volume of a Kilogramme of Saturated Steam in Cubic metres.		
	Values previously obtained.	By Equation (45).	By Experiment.
58·21°	8·38	8·23	8·27
68·52	5·41	5·29	5·33
70·76	4·94	4·83	4·91
77·18	3·84	3·74	3·72
77·49	3·79	3·69	3·71
79·40	3·52	3·43	3·43
83·50	3·02	2·94	3·05
86·83	2·68	2·60	2·62
92·66	2·18	2·11	2·15
117·17	0·991	0·947	0·941
118·23	0·961	0·917	0·906
118·46	0·954	0·911	0·891
124·17	0·809	0·769	0·758
128·41	0·718	0·681	0·648
130·67	0·674	0·639	0·634
131·78	0·654	0·619	0·604
134·87	0·602	0·569	0·583
137·46	0·562	0·530	0·514
139·21	0·537	0·505	0·496
141·81	0·502	0·472	0·457
142·36	0·495	0·465	0·448
144·74	0·466	0·437	0·432

This table shews that the values given by experiment agree much better with those calculated by the author's equation than with the values previously obtained; and that the experimental values are in general yet further removed from those previously obtained than are the values derived from the author's formula.

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* *Proc. Royal Soc.* 1860, and *Phil. Mag.*, Series IV. Vol. XXI.

§ 10. *Determination of the Mechanical Equivalent of Heat from the behaviour of Saturated Steam.*

Since we have determined the absolute values of s, without assuming the mechanical equivalent of heat to be known, we may now apply these values, by means of equation (17), to determine the mechanical equivalent itself. For this purpose we may give that equation the following form:

$$E = \frac{(a+t)\frac{dp}{dt}}{r}(s-\sigma) \quad \text{..............} (46).$$

The coefficient of $s-\sigma$ in this equation may be calculated for different temperatures by means of Regnault's tables. For example, to calculate its values for 100°, we have given for $\frac{dp}{dt}$ the value 27·20, the pressure being reckoned in millimetres of mercury. To reduce this to the measure here employed, viz. kilogrammes per square metre, we must multiply by the weight of a column of mercury at temperature 0°, 1 square metre in area and 1 millimetre in height, that is by the weight of 1 cubic decimetre of mercury at 0°. As Regnault gives this weight at 13·596 kilogrammes, the multiplication gives us the number 369·8. The values of $(a+t)$ and of r at 100° are 373 and 536·5 respectively. Hence we have

$$\frac{(a+t)\frac{dp}{dt}}{r} = \frac{373 \times 369{\cdot}8}{536{\cdot}5} = 257\,;$$

and equation (46) becomes

$$E = 257\,(s-\sigma) \text{.....................} (47).$$

We have now to determine the quantity $(s-\sigma)$, or, since σ is known, the quantity s for steam at 100°. The method formerly pursued, i.e. to use for saturated steam the same specific weight, which for superheated steam had been found by experiment or deduced theoretically from the condensation of water, led to the result, that a kilogram of steam at 100° should have a volume of 1·696 cubic metres. From the foregoing however it appears that this value must be considerably too large, and must therefore give too large a value for the mechanical equivalent of heat. Taking the specific heat as calculated by equation (45), which for 100° is 0·645, we obtain for s the value 1·638. Applying this value of s we get from equation (47)

$$E = 421 \qquad\qquad (48).$$

This method therefore gives for the mechanical equivalent of heat a value which agrees in a very satisfactory manner with the value found by Joule from the friction of water, and with that deduced in Chapter II. from the behaviour of gases; both of which are about equal to 424. This agreement may serve as a verification of the author's theory as to the density of saturated steam.

§ 11. *Complete Differential Equation for Q in the case of a body composed both of liquid and vapour.*

In § 1 of this chapter we expressed the two first differential coefficients of Q, for a body consisting both of liquid and vapour, by equations (7) and (8), as follows:

$$\frac{dQ}{dm} = \rho,$$

$$\frac{dQ}{dT} = m(H - C) + MC.$$

Hence we may form the complete differential equation of the first order for Q, as follows:

$$dQ = \rho dm + \Big[m(H - C) + MC\Big] dT \qquad\qquad (49).$$

By equation (12) we may put

$$H - C = \frac{d\rho}{dT} - \frac{\rho}{T},$$

whence equation (49) becomes

$$dQ = \rho dm + \left[m\left(\frac{d\rho}{dT} - \frac{\rho}{T}\right) + MC\right] dT \qquad\qquad (50).$$

Since ρ is a function of T only, and therefore

$$\frac{d\rho}{dT}dT = d\rho$$

we have $$dQ = d(m\rho) + \left(-\frac{m\rho}{T} + MC\right)dT \;\ldots\ldots\ldots(51),$$

or $$dQ = Td\left(\frac{m\rho}{T}\right) + MCdT \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots(52).$$

These equations are not integrable if the two quantities, whose differentials are on the right-hand side, are independent of each other, and the mode of the variations thus left undetermined. They become integrable as soon as this mode is determined in any way. We can then perform with them calculations exactly similar to those given for gases in Chapter II.

We will for the sake of example take a case which on the one hand has an importance of its own, and on the other derives an interest from the fact that it plays a prominent part in the theory of the steam-engine. The assumption is that the mass consisting both of liquid and vapour changes its volume, without any heat being imparted to it or taken from it. In this case the temperature and magnitude of the gaseous portion also suffers a change, and some external work, positive or negative, must at the same time be performed. The magnitude m of the gaseous portion, its volume v, and the external work W, must now be determined as functions of the temperature.

§ 12. *Change of the Gaseous Portion of the Mass.*

As the mass within the vessel can neither receive nor give off any heat, we may put $dQ = 0$. Equation (52) then becomes:

$$Td\left(\frac{m\rho}{T}\right) + MCdT = 0 \;\ldots\ldots\ldots\ldots\ldots(53).$$

If we divide this equation by E, the quantities ρ and C, which relate to the mechanical measure of heat, change into r and c, which relate to the ordinary measure of heat. If we also divide the equation by T, it becomes:

$$d\left(\frac{mr}{T}\right) + Mc\frac{dT}{T} = 0 \;\ldots\ldots\ldots\ldots\ldots(53a).$$

The first member of this equation is a simple differential, and may at once be integrated: the integration of the second is also always possible, since c varies only with the temperature T. If we merely indicate this integration, and denote the initial values of the various magnitudes by annexing the figure 1, we obtain the following equation:

$$\frac{mr}{T} - \frac{m_1 r_1}{T_1} + M \int_{T_1}^{T} c \frac{dT}{T} = 0,$$

or

$$\frac{mr}{T} = \frac{m_1 r_1}{T_1} - M \int_{T_1}^{T} c \frac{dT}{T} \quad \text{.................(54).}$$

Actually to perform the integration thus indicated, we may employ the empirical formula for c given by Regnault. For water this formula, already given in (27), is as follows:

$$c = 1 + 0{\cdot}00004 + 0{\cdot}0000009 t^2.$$

Since c is thus seen to vary very slightly with the temperature, we will in our calculations for water assume c to be constant, which will not seriously affect the accuracy of the results. Hence (54) becomes:

$$\frac{mr}{T} = \frac{m_1 r_1}{T} - Mc \log \frac{T}{T_1} \quad \text{.....................(55),}$$

whence

$$m = \frac{T}{r}\left(\frac{m_1 r_1}{T_1} - Mc \log \frac{T}{T_1}\right) \quad \text{........ ......(56).}$$

If we here substitute for r the expression given in (28), or in a simpler form in (30), then m will be determined as a function of temperature.

To give a general idea of the values of this function, some values have been calculated for a special case, and collected in the following table. The assumption is that the vessel contains at first no water in a liquid condition, but is filled with steam at its maximum density, so that in equation (56) we may put $m_1 = M$. Let there now be an expansion of the vessel. A compression would not be admissible, because on the assumption of the absence of water at the commencement, the steam would not remain at its maximum density, but would be superheated by the heat developed in the compression. In expansion on the other hand the steam not only remains at its maximum density, but a part of it is precipitated as water; and the diminution of m thus produced is exhibited in the table. The initial temperature is taken at 150° C., and the values of $\frac{m}{M}$ are given for the moments when the temperature has sunk through expansion to 125°, 100°, etc. As before, the temperature is reckoned from freezing point, and is denoted by t, to distinguish it from the absolute temperature T.

t	150°	125°	100°	75°	50°	25°
$\frac{m}{M}$	1	0·956	0·911	0·866	0·821	0·776

§ 13. *Relation between Volume and Temperature.*

To express the relation which exists between the volume v and the temperature, we may first apply equation (5):

$$v = mu + M\sigma.$$

The quantity σ, which expresses the volume of a unit of weight of the liquid, is a known function of temperature, and the same is therefore true of $M\sigma$. It remains to determine mu. For this purpose we need only substitute in equation (55) the expression for r given in equation (17). Thus we obtain

$$\frac{mu}{E} \times \frac{dp}{dT} = \frac{m_1 r_1}{T_1} - Mc \log \frac{T}{T_1} \text{ ....(57).}$$

whence

$$mu = \frac{E}{\frac{dp}{dT}} \left(\frac{m_1 r_1}{T_1} - Mc \log \frac{T}{T_1} \right) \text{ ....(58).}$$

The differential coefficient $\frac{dp}{dT}$ may be considered as known, since p is a known function of the temperature; and therefore this equation determines the product mu, and thence, by the addition of $M\sigma$, the required quantity v.

The following table gives a series of values of the quotient $\frac{v}{v_1}$, calculated by this equation for the same case as was treated in the last table. Under these are placed for the sake of comparison the values of $\frac{v}{v_1}$, which would hold if the two ordinary assumptions in the theory of the steam-engine were correct: viz. (1) that steam in expansion remains at its maximum density without any part of it condensing; (2) that steam follows the law of Mariotte and Gay-Lussac. On these assumptions we shall have

$$\frac{v}{v_1} = \frac{p_1}{p} \times \frac{T}{T_1}.$$

t	150^0	125^0	100^0	75^0	50^0	25^0
$\frac{v}{v_1}$	1	1·88	3·90	9·23	25·7	88·7
$\frac{p_1}{p} \times \frac{T}{T_1}$	1	1·93	4·16	10·21	29·7	107·1

§ 14. *Determination of the Work as a function of Temperature.*

It remains to determine the work done during the change of volume. For this we have the equation

$$W = \int_{v_1}^{v} pdv \text{ .... } (59).$$

But by equation (5), taking the magnitude σ (which is generally small and very slightly variable) as constant, we have:

$$dv = d\,(mu),$$

whence

$$pdv = pd\,(mu),$$

which may be also written thus

$$pdv = d\,(mup) - mu\frac{dp}{dT}dT \text{ .... } (60).$$

In this equation we may substitute for $mu\frac{dp}{dT}$ the expression given in equation (57), and may then perform the integration. The result however is obtained in a more convenient form as follows. By (13) we have:

$$mu\frac{dp}{dT}dT = \frac{m\rho}{T}dT;$$

and from (53) we obtain

$$\frac{m\rho}{T}dT = d(m\rho) + MCdT;$$

hence

$$mu\frac{dp}{dT}dT = d(m\rho) + MCdT.$$

Equation (60) now becomes

$$\begin{aligned} pdv &= d(mup) - d(m\rho) - MCdT \\ &= -d[m(\rho - up)] - MCdT \quad \text{............ (61).} \end{aligned}$$

Integrating this equation we obtain

$$W = m_1(\rho_1 - u_1p_1) - m(\rho - up) + MC(T_1 - T) \ \text{... (62).}$$

If in this equation we substitute for ρ and C, according to equation (14), the values Er and Ec, and collect together the terms which contain E as a factor, we have:

$$W = mup - m_1u_1p_1 + E[m_1r_1 - mr + Mc(T_1 - T)] \ \text{...(63).}$$

From this equation we may calculate W, since mr and mu are already known from the equations (56) and (58). This calculation has been made for the same case as before, and the values of $\frac{W}{M}$, i.e. of the work done by a unit of weight during expansion, are given in the following table; the unit of weight is here a kilogram and the unit of work a kilogrammetre. The value used for E is 423·55, as found by Joule.

As a comparison with the numbers of this table it may be again mentioned that the value obtained for the work done during the actual formation of steam, as this overcomes the external pressure, is 18700 kilogrammetres per kilogram of water, evaporated at temperature 150° and at the corresponding pressure.

t	150^0	125^0	100^0	75^0	50^0	25^0
$\frac{W}{M}$	0	11300	23200	35900	49300	63700

CHAPTER VII.

FUSION AND VAPORIZATION OF SOLID BODIES.

§ 1. *Fundamental Equations for the process of Fusion.*

Whilst in the case of vaporization the influence of the external pressure was early observed, and was everywhere taken into account, it had hitherto been left out of account in the case of fusion, where it is much less easily noticed. A little consideration however shews that, if the volume of a body changes during fusion, the external pressure must have an influence on the process. For, if the volume increases, an increase of pressure will make the fusion more difficult, whence it may be concluded that a higher temperature is necessary for fusion at a high than at a low pressure. If on the other hand the volume decreases, an increase of pressure will facilitate the fusion, and the temperature required will be less, as the pressure is greater.

To examine more exactly the connection between pressure and fusion-point, and the peculiar changes which are sometimes connected with a change of pressure, we must form the equations which are supplied for the process of fusion by the two fundamental principles of the Mechanical Theory of Heat. For this purpose we pursue the same course as for vaporization. We conceive an expansible vessel containing a certain quantity M of a substance, which is partly in the solid, and partly in the liquid condition. Let the liquid part have the magnitude m, and therefore the solid part the magnitude $M-m$. The two together are supposed to fill the vessel completely, so that the content of the vessel is equal to v, the volume of the body.

If this volume v and the temperature T are given, the magnitude m is thereby determined. To prove this, let us first suppose that the body expands during fusion. Let it be also in such a condition that the temperature T is exactly the melting temperature at that particular pressure. Now if in this condition the magnitude of the liquid part were to increase at the expense of the solid, the expansion which must then result would produce an increase of pressure against the walls of the vessel, and therefore an increased reaction of the walls against the body. This increased pressure would produce a rise in the fusion-point, and since the existing temperature would then be too low for fusion, a solidification of the liquid part must begin. If on the contrary the solid part were to increase at the expense of the liquid, the point of fusion would thereupon sink, and since the existing temperature would then be higher than the fusion-point, a fusion of the solid part must begin. Next, if we make the opposite assumption, viz. that the volume decreases during fusion, then if the solid part increase there must be a rise of pressure and in consequence a partial melting, and if the liquid part increase there must be a fall in pressure and in consequence a partial solidification. Thus on either assumption we have the same result, viz. that only the original proportions of the liquid and solid parts (which proportions correspond to the pressure which gives a temperature of fusion equal to the given temperature) can be permanently maintained. Since then the magnitude m is determined by the temperature and volume, this volume will conversely be determined by the temperature and the magnitude m; and we may choose T and m as the variables which serve to determine the condition of the body. It now remains to express p as a function of T. Here we may again apply equations (1), (2), (3) of the last chapter, viz.:

$$\frac{d}{dT}\left(\frac{dQ}{dm}\right)-\frac{d}{dm}\left(\frac{dQ}{dT}\right)=\frac{dp}{dT}\times\frac{dv}{dm},$$

$$\frac{d}{dT}\left(\frac{dQ}{dm}\right)-\frac{d}{dm}\left(\frac{dQ}{dT}\right)=\frac{1}{T}\times\frac{dQ}{dm},$$

$$\frac{dQ}{dm}=T\frac{dp}{dT}\times\frac{dv}{dm}.$$

If we denote by σ, as before, the specific volume (or volume of a unit of weight) for the liquid condition of the body, and the specific volume for the solid condition by τ, we have for the total volume v of the body,

$$v = m\sigma + (M - m)\tau,$$

or

$$v = m(\sigma - \tau) + M\tau \quad \text{.....................(1)},$$

whence

$$\frac{dv}{dM} = \sigma - \tau \quad \text{.....................(2)}.$$

If further we denote the heat of fusion for a unit of weight by ρ', we may put

$$\frac{dQ}{dm} = \rho' \quad \text{.........................(3)}.$$

To express $\frac{dQ}{dT}$, the other differential coefficient of Q, we must employ symbols for the specific heat of the body in the liquid and in the solid condition. Here, however, we must make the same remark as in the case of vaporization, viz. that it is not the specific heat at constant pressure which is treated of, but the specific heat for the particular case in which the pressure alters with the temperature in such a way that the temperature shall always be the temperature of fusion for that particular pressure. In the case of vaporization, where the changes of pressure are generally small, it was possible to neglect the influence of the change of pressure on the specific heat of the liquid body, and to consider the specific heat of a liquid body, as found in the formula, to be equivalent to the specific heat at constant pressure. In the present case small changes of temperature produce such great changes of pressure, that the influence of these on the specific heat must not be neglected. We will, therefore, under the present circumstances, denote by C' the specific heat of the liquid, which in the formula for vaporization we denoted by C. The specific heat of the solid body may be denoted in this case by K'. Applying these symbols we may write

$$\frac{dQ}{dT} = mC' + (M - m)K',$$

or

$$\frac{dQ}{dT} = m(C' - K') + MK' \quad \text{.............(4)}.$$

From equations (3) and (4) we have

$$\frac{d}{dT}\left(\frac{dQ}{dm}\right)=\frac{d\rho'}{dT}\ldots\ldots\ldots\ldots(5),$$

$$\frac{d}{dm}\left(\frac{dQ}{dT}\right)=C'-K'\ldots\ldots\ldots\ldots(6).$$

Inserting these values, and the value for $\frac{dQ}{dm}$ given in (3), in the above differential equations, we obtain

$$\frac{d\rho'}{dT}+K'-C'=(\sigma-\tau)\frac{dp}{dT}\ldots\ldots\ldots\ldots(7),$$

$$\frac{d\rho'}{dT}+K'-C'=\frac{\rho'}{T}\ldots\ldots\ldots\ldots(8),$$

$$\rho'=T(\sigma-\tau)\frac{dp}{dT}\ldots\ldots\ldots\ldots(9).$$

In these equations the heat is supposed to be measured by mechanical units. If the heat is to be measured in ordinary units, we may use the following symbols:

$$c'=\frac{C'}{E};\quad k'=\frac{K'}{E};\quad r'=\frac{\rho'}{E}\ldots\ldots\ldots\ldots(10).$$

The equations then become

$$\frac{dr'}{dT}+k'-c'=\frac{\sigma-\tau}{E}\left(\frac{dp}{dT}\right)\ldots\ldots\ldots\ldots(11),$$

$$\frac{dr'}{dT}+k'-c'=\frac{r'}{T}\ldots\ldots\ldots\ldots(12),$$

$$r=\frac{T(\sigma-\tau)}{E}\left(\frac{dp}{dT}\right)\ldots\ldots\ldots\ldots(13).$$

These are the equations required, of which the first corresponds to the first Fundamental Principle, and the second to the second, whilst the third is a combination of the other two.

§ 2. *Relation between Pressure and Temperature of Fusion.*

The foregoing equations, only two of which are independent, may be applied to determine two quantities hitherto unknown.

We will first use the last equation to determine the way in which the temperature of fusion depends on the pressure. The equation may be written

$$\frac{dT}{dp} = \frac{T(\sigma - \tau)}{Er'} \text{ .... } (14).$$

This equation in the first place justifies the remark already made, that if a body expand during fusion the point of fusion rises as the pressure increases; whereas if the body contracts the point of fusion falls. For according as σ is greater or less than τ so is the difference $\sigma - \tau$, and therefore also the differential coefficient $\frac{dT}{dp}$, positive or negative. Again, by this equation we may calculate the numerical value of $\frac{dT}{dp}$. We will calculate this value for the case of water. The volume in cubic metres, or the value of σ, for a kilogramme of water at 4° C. is 0·001. At freezing point it is a little greater, but the difference is so small that it may be neglected. The volume in cubic metres, or the value of τ, for a kilogram of ice is 0·001087. The heat of fusion for water, or the value of r', is according to Person 79. At freezing point T equals 773, and for E we will take the value 424. Hence we obtain

$$\frac{dT}{dp} = -\frac{273 \times 0{\cdot}000087}{424 \times 79}.$$

If the pressure is given not in mechanical units (kilograms per square metre), but in atmospheres, we must multiply the above value of $\frac{dT}{dp}$ by 10333. This gives us

$$\frac{dT}{dp} = -0{\cdot}00733,$$

i.e. an increase of pressure of one atmosphere will lower the point of fusion by 0·00733 of a degree Cent.

§ 3. *Experimental Verification of the Foregoing Result.*

The conclusion that the melting point of ice is lowered by an increase of pressure, and the first calculation of the amount, are due to James Thomson, who derived from Carnot's theory an equation which differs from our equation (14) only in this, that in the place of $\frac{T}{E}$ it contains an unknown function of temperature, whose particular value for the freezing point was determined from Regnault's data on the heat of vaporization and pressure of steam. Sir William Thomson afterwards applied to this theoretical result a very accurate test by experiment*.

In order to measure small differences of temperature, he prepared a thermometer filled with ether-sulphide, the bulb of which was 3½ in. long and the tube 6½ in. Of this 5½ in. were divided in 220 equal parts, and 212 of these parts comprised an interval of temperature of 3° Fahr., so that each part was about equal to $\frac{1}{71}$ of a degree Fahr. This thermometer was hermetically enclosed in a larger glass tube, to protect it from the external pressure, and so enclosed was placed in an Oersted press, filled with water and lumps of clear ice, and containing an ordinary air gauge to measure the pressure. When the thermometer had become stationary at a point corresponding to the melting point of ice at atmospheric pressure, the pressure was increased by screwing down the press. The thermometer was at once seen to fall, as the mass of water and ice assumed the lower melting temperature corresponding to the higher pressure. On taking off this pressure the thermometer returned to its original position. The table below gives the fall of temperature observed for two different pressures, and also the fall of temperature, as calculated for those same pressures by applying to temperatures

Pressure.	Fall of Temperature.	
	Observed.	Calculated.
8·1 Atm.	0·059° C.	0·059° C.
16·8 „	0·129 „	0·123 „

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* *Phil. Mag.*, Series III. Vol. XXXVII. p. 123.

as high as 16·8 atm. the value of $\frac{dT}{dp}$, which was found in the last section, and which primarily relates to the ordinary atmospheric pressure.

We see that the observed and calculated numbers agree very closely together, and thus another result of theory has been verified by experiment.

More recently a very striking experiment was performed by Mousson*, who by the application of enormous pressures melted ice which was kept during the experiment at a temperature of $-18°$ to $-20°$. The pressure employed he calculates approximately at about 13000 atmospheres; on which it may be remarked that it may be possible to produce the melting with a much smaller pressure, since with his arrangement all that could be known was that the ice had somehow melted during the experiment, and not the exact time at which the melting took place.

§ 4. *Experiments on Substances which expand during Fusion.*

Bunsen† was the first to institute experiments on substances which expand during fusion, and of which the fusion point must therefore rise as the temperature increases. The substances he chose were spermaceti and paraffin. By an ingenious arrangement he obtained in an extremely simple manner a very high and at the same time measurable increase of pressure, and was able to observe portions of the same substance side by side under ordinary atmospheric, and under the increased pressure. He took a tube of thick glass about the size of a straw and 1 foot in length, and drew it at one end into a capillary tube 15 to 20 inches long, and at the other end into a somewhat larger one only 1½ inches long. The latter, which was placed lowest in the apparatus, was bent round until it stood up parallel to the lower part of the glass tube. This short curved part was filled with the substance to be tested, and the larger glass tube with quicksilver, whilst the long capillary tube remained filled with air. Both capillary tubes were sealed at the ends. On heating the apparatus the quicksilver expanded, rose in the longer capillary tube, and compressed the air within it. The reaction of this air compressed first the quicksilver and then the substance in the shorter tube, and the magnitude of the pressure, which was capable of rising to above 100 atmospheres, could be measured by the volume of air left in the upper tube.

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* Pogg. *Ann.*, Vol. cv. p. 161.

† Pogg. *Ann.*, Vol. LXXXI. p. 562.

This apparatus was fixed on a board close to another arranged in the same way except that the upper air-tube was not sealed; so that no compression of the air, and consequent rise of pressure, could take place. The two tubes were now plunged in water, the temperature of which was somewhat higher than the melting point of the substance to be tested. Thus when the lower tube filled with the substance was once completely under water, it was only needed to sink it still deeper in order to heat a larger part of the quicksilver, and so to obtain a higher pressure in the closed upper tube. Under these conditions Bunsen repeatedly melted the substance in both tubes, and then by cooling the water allowed it again to solidify, observing the temperature at which this took place. The result was that this solidification always took place at a higher temperature in the tube in which the pressure was increased than in the other. The following were the numerical results.

Spermaceti.

Pressure.	Point of Solidification.
1 Atm.	47·7° C.
29 „	48·3 „
96 „	49·7 „
141 „	50·5 „
156 „	50·9 „

Paraffin.

Pressure.	Point of Solidification.
1 Atm.	46·3° C.
85 „	48·9 „
100 „	49·9 „

More recently Hopkins* experimented with spermaceti, wax, sulphur, and stearine, producing pressures by means of a weighted lever to 800 atmospheres and upwards. With all the above substances a rise of the melting point under an increase of pressure was observed. The particular temperatures observed with different pressures shewed however considerable irregularities. In the case of wax, with which the rise of temperature was most regular, an increase of pressure of 808 atmospheres produced a rise in the melting point of 15½° Cent.

The calculation of the rise in the melting point from the theoretical formula cannot well be performed for the substances tested by Bunsen and Hopkins, since the data required are not known with sufficient accuracy.

§ 5. *Relation between the heat consumed in Fusion and the temperature of Fusion.*

Having applied equation (13), in § 2, to determine the relation between the temperature of fusion and the pressure, we will now turn to equation (12), which may be written as follows:

$$\frac{dr'}{dT} = c' - k' + \frac{r'}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots (15).$$

This equation shews that, if the temperature of fusion is changed by a change of pressure, the quantity of heat r' required for fusion also changes. The amount of this change can be determined from the equation. In this the symbols c' and k' denote the specific heat of the substance in the liquid and in the solid condition, not however, as already observed, the specific heat at constant pressure, but the specific heat in the case in which the pressure changes with the temperature in the manner indicated by equation (13).

The mode of determining this kind of specific heat will be described in the next chapter. Here we will merely by way of example give the numerical values in the case of water. The specific heat at constant pressure, i.e. that specific heat which is simply measured at atmospheric pressure, has in the neighbourhood of 0° the value 1 for water, and, according to Person†, the value 0·48 for ice.

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* *Report, Brit. Assoc.*, 1854, p. 57.

† *Comptes Rendus*, Vol. xxx. p. 526.

The specific heat for the case here considered has on the contrary for water and ice the values $c'=0{\cdot}945$ and $k'=0{\cdot}631$. For r' we may take Person's value 79. We thus obtain

$$\begin{aligned}\frac{dr'}{dT} &= 0{\cdot}945 - 0{\cdot}631 + \frac{79}{273}\\ &= 0{\cdot}314 + 0{\cdot}289\\ &= 0{\cdot}603.\end{aligned}$$

It is known that the freezing point of water can also be lowered by protecting it from every sort of disturbance. This lowering of temperature however only refers to the commencement of freezing. As soon as this has begun, a portion of the water freezes immediately such that the whole mass of water is thereby warmed again up to 0°, and the remainder of the freezing takes place at that temperature. There is therefore no need to examine more closely the change in the magnitude r' which corresponds to a lowering of the temperature of this kind, and which is simply determined by the difference of the specific heat of water and ice at constant pressure.

§ 6. *Passage from the solid to the gaseous condition.*

Hitherto we have considered the passage from the liquid to the gaseous and from the solid to the liquid condition. It may however happen that a substance passes direct from the solid to the gaseous condition. In this case three equations will hold of the same form as equations (15), (16) and (17) of the last chapter, or (11), (12), (13) of this: we must only remember to choose the specific heats and specific volumes relating to the different states of aggregation, and the quantities of heat consumed in the passage from one condition to the other, in the manner corresponding to the present case.

The circumstance that the heat expended is greater in the passage from the solid condition to the gaseous than from the liquid, leads to a conclusion which has already been drawn by Kirchhoff*. For if we consider a substance when just at its melting point, vapour may be developed at this temperature both from the liquid and from the solid. At temperatures above the melting point we have only to do with vapour developed from a liquid, and at temperatures below with vapour developed from a solid, leaving out of account the special case mentioned in the last section, in which a liquid kept perfectly still remains fluid in spite of having reached a lower temperature.

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* *Pogg. Ann.*, Vol. CIII. p. 206.

If for these two cases, i.e. for temperatures above and below the melting point, we express the pressure of vapour p as a function of temperature, and construct for each case the curve which has the temperatures for abscissæ and the pressures for ordinates, the question arises how the curves corresponding to the two cases are related to each other at the common limit, viz. the temperature of fusion. In the first place, so far as concerns the value of p itself, we may consider it as known by experience to be equal in the two cases; and thus the two curves will meet in one point at the temperature of fusion. But with regard to the differential coefficient $\frac{dp}{dT}$, the last of the above-named three equations shews that it has different values in the two cases; and thus the tangents to the two curves at their point of intersection have different directions.

Equation (17) of Chapter VI. which relates to the passage from the liquid to the gaseous condition, may be written as follows:

$$\frac{dp}{dT} = \frac{Er}{T(s-\sigma)} \qquad (16).$$

To form the corresponding equation for the passage from the solid to the gaseous condition, we should set on the left hand the pressure of the vapour given off by the solid body, which for distinction we may call P. On the right hand we must put, instead of σ, which is the specific volume of the liquid, the specific volume of the solid which we may call τ; the difference thus indicated is however very small, since these two specific volumes differ very slightly from each other, and in addition are small in comparison with s, the specific volume of the substance as a gas. It is of more importance to substitute for r, which is the heat required to cause the passage from the liquid to the gaseous condition, the quantity of heat required for the passage from the solid to the gaseous condition. This latter equals $r+r'$, where r' is the heat required for melting. Thus in the present case the equation is:

$$\frac{dP}{dT}=\frac{E(r+r')}{T(s-\tau)} \qquad\text{.......................(17).}$$

Combining this equation with (16), and neglecting the small difference between σ and τ, we have

$$\frac{dP}{dT}-\frac{dp}{dT}=\frac{Er'}{T(s-\sigma)} \qquad\text{......................(18).}$$

If we apply this equation to water, we must put $T=273$, $r'=79$, $s=205$, $\sigma=0{\cdot}001$, and giving E the known value 424 we have

$$\frac{dP}{dT}-\frac{dp}{dT}=\frac{424\times 79}{273\times 205}=0{\cdot}599.$$

If we wish to express the pressure in millimetres of mercury, instead of kilogrammes per square metre, we must, as remarked in Chapter VI. § 10, divide the above result by 13·596; then putting for p and P the Greek letters π and Π, we have

$$\frac{d\Pi}{dT}-\frac{d\pi}{dT}=0{\cdot}044.$$

It may be added for the sake of comparison that the differential coefficient $\frac{d\pi}{dT}$ has for 0° the value 0·33, according to the pressures which Regnault has observed at temperatures just over 0°.

CHAPTER VIII.

ON HOMOGENEOUS BODIES.

§ 1. *Changes of Condition without Change in the Condition of Aggregation.*

We will now return to the general equations of Chapter V. and will apply them to cases, in which a body undergoes changes which do not extend so far as to alter its condition of aggregation, but in which all parts of the body are always in the same condition. We will suppose these changes to be produced by changes in the temperature and in the external pressure. In consequence of these, changes take place in the arrangement of the molecules of the body, which are indicated by changes in form and volume.

With regard to the external force, the simplest case is that in which an uniform normal pressure alone acts on the body; in this case no account need be taken of changes in the body's form, in determining the external work, but only of its alteration in volume. Here we may take the condition of the body as known, if of the three magnitudes, temperature, pressure and volume, which we will denote as before by T, p and v, any two are given. According as we choose for this purpose v and T, or p and T, or v and p, so we obtain one of the three systems of equations, which in Chapter V. are numbered (25), (26) and (27): these equations we will now use to determine the different specific heats and other quantities, related to changes in temperature, pressure, and volume.

§ 2. *Improved Denotation for the Differential Coefficients.*

If the above-named equations of Chapter V. are referred to a unit of weight of the substance, the differential coefficient $\frac{dQ}{dT}$ will denote in equations (25) the specific heat at constant volume, and in equations (26) the specific heat at constant pressure. Similarly $\frac{dQ}{dv}$ has different values in (25) and (27) and $\frac{dQ}{dp}$ has different values in (26) and (27). Such indeterminate cases always occur where the nature of the question occasions the magnitudes chosen as independent variables to be sometimes interchanged. If we have chosen any two magnitudes as independent variables, it follows that in differentiating according to one we must take the other as constant. But if, whilst keeping the first of these as one independent variable throughout, we then choose for the other different magnitudes in succession, we naturally arrive at a corresponding number of different significations for the differential coefficients taken according to the first variable.

This fact induced the author, in his paper "On various convenient forms of the fundamental equations of the Mechanical Theory of Heat,"* to propose a system of denotation which so far as he knows had not been in use before. This was to subjoin to the differential coefficient as an index the magnitude which was taken as constant in differentiating. For this purpose the differential coefficient was inclosed in brackets and the index written close to it, a line being drawn above the latter, to distinguish it from other indices, which might appear at the same place. The two differential coefficients named above, which represent the specific heat at constant volume and at constant pressure, would thus be written respectively $\left(\frac{dQ}{dT}\right)_{\bar{v}}$ and $\left(\frac{dQ}{dT}\right)_{\bar{p}}$. This method was soon adopted by various writers, but the line was generally left out for the sake of convenience. More recently* the author introduced a simpler form of writing, which yet retained the essential advantage of the method. This consisted in placing the index next to *d*, the sign of differentiation. The brackets were thus rendered needless and also the horizontal line, because no other index is in general placed in this position. The two above-named differential coefficients would thus be written $\frac{d_vQ}{dT}$ and $\frac{d_pQ}{dT}$; and this method will be adopted in what follows.

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* *Report of the Naturalists' Society of Zurich*, 1865, and Pogg. *Ann.*, Vol. cxxv. p. 353.

§ 3. *Relations between the Differential Coefficients of Pressure, Volume, and Temperature.*

If the condition of the body is determined by any two of the magnitudes, Temperature, Volume, and Pressure, we may consider each of these as a function of the two others, and thus form the following six differential coefficients:

$$\frac{d_vp}{dT},\ \frac{d_Tp}{dv},\ \frac{d_pv}{dT},\ \frac{d_Tv}{dp},\ \frac{d_pT}{dv},\ \frac{d_vT}{dp}.$$

In these the suffixes, which shew which magnitude is to be taken as constant, may be omitted, provided we agree once for all that in any differential coefficient that one of the three magnitudes, T, p, v, which does not appear, is to be considered as constant for that occasion. We shall however retain them for the sake of clearness, and because we shall meet with other differential coefficients between the same magnitudes, for which the constant magnitude is not the same as here.

The investigations to be made by help of these six differential coefficients will be facilitated, if the relations which exist between them are laid down beforehand. In the first place it is clear that amongst the six there are three pairs which are the reciprocals of each other. If we take v as constant, T and p will then be so connected that each may be treated as a simple function of the other. The same holds with T and v where p is constant, and with v and p when T

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* "On the principle of the Mean Ergal and its application to the molecular motions of Gases." *Proceedings of the Niederrhein. Ges. für Natur- und Heilkunde*, 1874, p. 183.

is constant. Hence we may put

$$\frac{1}{\dfrac{d_vT}{dp}}=\frac{d_vp}{dT};\quad \frac{1}{\dfrac{d_pT}{dv}}=\frac{d_pv}{dT};\quad \frac{1}{\dfrac{d_Tp}{dv}}=\frac{d_Tv}{dp}\;\ldots\ldots\ldots\ldots(1).$$

To examine further the relation between these three pairs, we will by way of example treat p as a function of T and v. Then the complete differential equation for p is

$$dp=\frac{d_vp}{dT}\,dT+\frac{d_Tp}{dv}\,dv.$$

If p is constant, we must put in this equation,

$$dp=0,\quad dv=\frac{d_pv}{dT}\,dT;$$

whence it becomes

$$0=\frac{d_vp}{dT}\,dT+\frac{d_Tp}{dv}\,\frac{d_pv}{dT}\,dT:$$

whence

$$\frac{d_Tp}{dv}\times\frac{d_pv}{dT}\times\frac{d_vT}{dp}=-1\;\ldots\ldots\ldots\ldots\ldots\ldots(2).$$

By means of this equation combined with equations (1), we may express each of the six differential coefficients by the product or the quotient of two other differential coefficients.

§ 4. *Complete Differential Equations for* Q.

We will now return to the consideration of the heat taken in and given out by the body. If we denote the specific heat at constant volume by C_v, and at constant pressure by C_p, and take the weight of the body as unity, we have

$$\frac{d_vQ}{dT}=C_v;\quad \frac{d_pQ}{dT}=C_p.$$

We have also the equations (25) and (26) of Chapter V., which with our present notation will be written as follows:

$$\frac{d_TQ}{dv}=T\frac{d_vp}{dT};\quad \frac{d_TQ}{dp}=-T\frac{d_pv}{dT}.$$

Hence we can write down the following complete differential equations:

$$dQ = C_v dT + T\frac{d_v p}{dT}dv \ldots\ldots\ldots\ldots\ldots\ldots(3),$$

$$dQ = C_p dT - T\frac{d_p v}{dT}dp \ldots\ldots\ldots\ldots\ldots\ldots(4).$$

From these two we easily obtain a third differential equation for Q, which relates to v and p as independent variables. For multiplying the first equation by C_p and the second by C_v, subtracting, and dividing the result by $C_p - C_v$, we have

$$dQ = \frac{T}{C_p - C_v}\left(C_p \frac{d_v p}{dT}dv + C_v \frac{d_p v}{dT}dp\right) \ldots\ldots\ldots(5).$$

These three equations correspond exactly to those obtained in Chapter II. for perfect gases, except that the latter are simplified by applying the law of Mariotte and Gay-Lussac. The equation expressing this law is

$$pv = RT,$$

whence we have

$$\frac{d_v p}{dT} = \frac{R_v}{v}; \quad \frac{d_p v}{dT} = \frac{R}{p}.$$

Substituting these values in the above equations, and in the last putting $\frac{pv}{R}$ for T, we get

$$dQ = C_v dT + \frac{RT}{v}dv,$$

$$dQ = C_p dT - \frac{RT}{p}dp,$$

$$dQ = \frac{C_p}{C_p - C_v}pdv + \frac{C_v}{C_p - C_v}vdp.$$

These equations are the same as (11), (15) and (16) of Chapter II.

The equations (3), (4) and (5) are not immediately integrable, as has been already shewn with respect to the special equations holding for gases. For equations (3) and (4) this follows from equations already given. If in the last equations of the systems (25) and (26) of Chapter V. we use the symbols C_v and C_p, and also the method above explained of writing the differential coefficients, we have

$$\frac{d_T C_v}{dv} = T\frac{d_v^2 p}{dT^2}; \quad \frac{d_T C_p}{dp} = -T\frac{d_p^2 v}{dT^2} \text{...........(6).}$$

Whereas the conditions which must be fulfilled, if (3) and (4) are to be integrable, are as follows:

$$\frac{d_T C_v}{dv} = T\frac{d_v^2 p}{dT^2} + \frac{d_v p}{dT}; \quad \frac{d_T C_p}{dp} = -T\frac{d_p^2 v}{dT^2} - \frac{d\ v}{dT}.$$

By a similar but longer process we may shew that equation (5) is not integrable; as may at once be concluded from the fact that it is derived from equations (3) and (4).

These three equations thus belong to that class of complete differential equations which are described in the Introduction, and which can only be integrated if a further relation between the variables is given, and the path of the variation thereby fixed.

§ 5. *Specific Heat at Constant Volume and at Constant Pressure.*

If in equation (4) we substitute for the indeterminate differential dp the expression $\frac{d_v p}{dT} dT$, we introduce the special case in which the body changes its temperature by dT, the volume remaining constant. If we divide by dT we have on the left-hand side the differential coefficient $\frac{d_v Q}{dT}$, which is the specific heat at constant volume and has been denoted by C_v. Hence we obtain the following relation between C_v and C_p:

$$C_v = C_p - T\frac{d_p v}{dT} \times \frac{d_v p}{dT} \text{......................(7).}$$

Substituting in equation (5) the value of $C_p - C_v$ given by this equation, we obtain the following simpler form:

$$dQ = C_p \frac{d_p T}{dv} dv + C_v \frac{d_v T}{dp} dp \text{..............(8).}$$

If by means of equation (7) we proceed to determine the specific heat at constant volume from that at constant pressure, it is requisite first to make a slight change in the equation. The differential coefficient $\frac{d_p v}{dT}$ contained therein expresses the expansion of the body upon a rise of temperature, and may generally be taken as known, but the other differential coefficient $\frac{d_v p}{dT}$ cannot in general be determined for solid and liquid bodies by direct experiment. However from equation (2) we have

$$\frac{d_v p}{dT} = -\frac{\frac{d_p v}{dT}}{\frac{d_T v}{dp}}.$$

In this fraction the numerator is the differential coefficient already discussed, and the denominator expresses, if taken with a negative sign, the diminution of volume by an increase of pressure, or the compressibility of the body; and this for a large number of liquids has been directly measured, whilst for solids it may be approximately calculated from the coefficients of elasticity. Equation (7) now becomes

$$C_v = C_p + T\frac{\left(\frac{d_p v}{dT}\right)^2}{\frac{d_T v}{dp}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (7a).$$

If the specific heats are expressed not in mechanical but in ordinary units, we may denote them by c_v and c_p; the equation then takes the form:

$$c_v = c_p + \frac{T}{E}\frac{\left(\frac{d_p v}{dT}\right)^2}{\frac{d_T v}{dp}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (7b).$$

In applying this equation to a numerical calculation we must remember, that in the differential coefficients the unit of volume must be the cube of the unit of length which has been used for determining E: and that the unit of pressure must be the pressure which a unit of weight exerts on a unit of surface. If, as is usually the case, the coefficients of expansion and compression refer to other units, they must be reduced to those above mentioned.

Since the differential coefficient $\frac{d_T v}{dp}$ is always negative, the specific heat at constant volume must always be less than that at constant pressure. The other differential coefficient $\frac{d_p v}{dT}$ is generally positive. In the case of water it is zero at the temperature of maximum density, and accordingly the two specific heats are equal at that temperature. At all other temperatures, both above and below, the specific heat at constant volume is less than that at constant pressure; for although the differential coefficient $\frac{d_p v}{dT}$ is negative below the temperature of maximum density, yet, as it is the square of this which occurs in the formula, it has no influence on its value.

As an example of the application of equation (7), we will calculate the difference between the two specific heats in the case of water at certain known temperatures. According to the observations of Kopp (see his tables in *Lehrbuch der Phys. u. theor. Chimie*, p. 204), we have the following coefficients of expansion in the case of water, its volume at 4° being taken as unity:

at	0°	−0·000061,
„	25°	+0·00025,
„	50°	+0·00045.

According to the observations of Grassi*, we have for the compressibility of water the following numbers, which express the diminution of volume upon an increase of pressure of one atmosphere, in the form of a decimal of the volume at the original pressure:

at	0°	0·000050,
„	25°	0·000046,
„	50°	0·000044.

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* *Ann. de Chim. et de Phys.* 3rd ser. Vol. XXXI. p. 437, and Krönig's *Journ. für Physik des Auslandes*, Vol. II. p. 129.

We will now, as an example, perform the calculation for the temperature of 25°. The unit of length may be the metre, the unit of weight the kilogram. We must then take the cubic metre as the unit of volume; and, since a kilogram of water at 4° contains 0·001 cubic metres, we must, in order to obtain $\frac{d_p v}{dT}$, multiply the coefficient of expansion given above by 0·001. Thus we have

$$\frac{d_p v}{dT} = 0{\cdot}00000025 = 25 \times 10^{-8}.$$

For compression we must, by what has been said, take as unit the volume which the water contained at the temperature in question and at the original pressure (which latter we may assume to be the ordinary pressure of one atmosphere). This volume at $25° = 0{\cdot}001003$ cubic metres. Further we have taken one atmosphere as unit of pressure, whereas we must take the pressure of 1 kilogramme on 1 square metre; in which case a pressure of one atmosphere is expressed by 10,333. Accordingly, we must put

$$\frac{d_T v}{dp} = -\frac{0{\cdot}000046 \times 0{\cdot}001003}{10{,}333} = -45 \times 10^{-13}.$$

Further, we have at 25°, $T = 273 + 25 = 298$; and for E we will take Joule's value 424. Substituting these numbers in equation (7*b*), we get

$$c_p - c_v = \frac{298}{424} \times \frac{25^2}{45} \times \frac{10^{-16}}{10^{-13}} = 0{\cdot}0098.$$

In the same way we obtain from the values given above for the coefficients of expansion and compression at 0° and 50° the following numbers:

$$\begin{aligned} &\text{at } \ 0°, \ c_p - c_v = 0{\cdot}0005, \\ &\text{,, } \ 50°, \ c_p - c_v = 0{\cdot}0358. \end{aligned}$$

If we now give to c_p, or the specific heat at constant pressure, the experimental values found by Regnault, we obtain for the two specific heats the following pairs of values:

$$\text{at}\quad 0^\circ \begin{cases} c_p = 1 \\ c_v = 0{\cdot}9995, \end{cases}$$

$$,,\quad 25^\circ \begin{cases} c_p = 1{\cdot}0016 \\ c_v = 0{\cdot}9918, \end{cases}$$

$$,,\quad 50^\circ \begin{cases} c_p = 1{\cdot}0042 \\ c_v = 0{\cdot}9684. \end{cases}$$

§ 6. *Specific Heats under other circumstances.*

In the same way as we have determined the specific heat at constant volume in the last section, we may determine also the specific heat corresponding to various other circumstances, since we may by equation (4) fix its relation to the specific heat at constant pressure.

Thus, if the circumstances are given under which the heating takes place, the two differentials dT and dp are no longer independent, but the one is determined by the other. We can therefore write for dp the product $\frac{dp}{dT}dT$, in which $\frac{dp}{dT}$ is a known function of the variables on which the condition of the body depends. Substituting this product for dp in equation (4), dividing by dT, and denoting by C the quotient $\frac{dQ}{dT}$, which stands on the left-hand side of the equation, and which expresses the specific heat under the given circumstances, we obtain

$$C = C_p - T\frac{d_p v}{dT} \times \frac{dp}{dT} \quad\text{..................}(9).$$

If the specific heat is to be expressed in ordinary units, we may use the symbol c instead of C; and the equation becomes

$$c = c_p - \frac{T}{E}\cdot\frac{d_p v}{dT}\cdot\frac{dp}{dT} \quad\text{.................. }(9a).$$

We will employ this equation, by way of example, to determine the specific heats which came under consideration in the two last chapters, viz. (1) the specific heat of water, when in contact with steam at maximum pressure; (2) the specific heat of water and ice, when the pressure changes with the temperature in such a way that the temperature of melting corresponding to the pressure at any moment is always equal to the temperature which exists at that moment.

In the first case we have simply to give to $\frac{dp}{dT}$ the value corresponding to the intensity of pressure of the steam. For the temperature 100° this value is 370, taking as unit of pressure a kilogram per square metre. With regard to $\frac{d_pv}{dT}$, the researches of Kopp give 0·00080 as the coefficient of expansion of water at 100°, taking the volume of water at 4° as unity. This number must be multiplied by 0·001, in order to obtain the value of $\frac{d_pv}{dT}$ in the case when a cubic metre is taken as the unit of volume and a kilogram as the unit of weight: we thus obtain the number 0·0000008. Lastly we write for T the absolute temperature for 100°, or 373, and for E, as usual, 424. Then equation (9a) becomes

$$c = c_p - \frac{373}{424} \times 0{\cdot}0000008 \times 370 = c_p - 0{\cdot}00026.$$

If we take for the specific heat of water at constant pressure, and at 100°, the values derived from the empirical formula of Regnault, we obtain for the two specific heats which we wish to compare, the following simultaneous values:

$$c_p = 1{\cdot}013,$$
$$c = 1{\cdot}01274.$$

It thus appears that these two quantities are so nearly equal, that it would have been useless to take account of the difference between them in the calculations as to saturated steam.

The consideration of the influence of pressure on the freezing point of liquids shews that a great change in the pressure only produces a very slight alteration in the freezing point; hence in this case $\frac{dp}{dT}$ must be very large. If we assume, according to the calculations in Chapter VII., that an increase of pressure of one atmosphere lowers the freezing point by 0·00733° C., we have

$$\frac{dp}{dT} = -\frac{10\,333}{0{\cdot}00733};$$

hence equation (9*a*) becomes, giving to T the value at the freezing point, viz. 273, and to E the value 424,

$$c = c_p + \frac{273}{424} \times \frac{10\,333}{0{\cdot}00733} \times \frac{d_p v}{dT} = c_p + 908000\,\frac{d_p v}{dT}.$$

Applying this equation first to water, we will take Kopp's value for the coefficient of expansion of water at 0°, viz. $-0{\cdot}000061$; then, using the kilogram as unit of weight, and the cubic metre as unit of volume, we have

$$\frac{d_p v}{dT} = -0{\cdot}000000061;$$

whence, from the equation above,

$$c = c_p - 0{\cdot}055.$$

As c_p is here $= 1$, being the ordinary heat unit, we have finally

$$c = 0{\cdot}945.$$

Next, to apply the equation to ice, we will take the linear coefficient of expansion of ice at 0·000051, following the experiments of Schumacher, Pohrt, and Moritz; whence the cubic coefficient will be 0·000153. In order to reduce this number to the required units, we must multiply it by 0·001087, the volume of a kilogram of ice in cubic metres: whence we obtain

$$\frac{d_p v}{dT} = 0{\cdot}000000166.$$

Substituting this value, the equation becomes

$$c = c_p + 0{\cdot}151.$$

According to Person* $c_p = 0{\cdot}48$: hence we have finally

$$c = 0{\cdot}631.$$

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* *Comptes Rendus*, Vol. xxx. p. 526.

These values, 0·945 and 0·631, were those employed in Chapter VII. for the calculation by which the relation between the heat expended in fusion and the temperature of fusion was determined.

§ 7. *Isentropic Variations of a Body.*

Instead of determining the kind of variation of condition, which a body is to undergo, by means of an equation containing one or more of the quantities T, p, v, we will now lay down as a condition, that no heat is imparted to or withdrawn from the body during its variation. This is expressed mathematically by the equation

$$dQ = 0.$$

If this equation holds, we have further

$$dS = \frac{dQ}{dT} = 0,$$

that is, the entropy S of the body remains constant. We will therefore give to this kind of variation the designation isentropic, already applied to the curves of pressure which correspond to it: and will characterize the differential coefficients formed in discussing it by the index S.

If in equation (3) we put $dQ = 0$, we have

$$0 = C_v dT + \frac{T d_v p}{dT} dv.$$

If we divide this equation by dv, the differential coefficient $\frac{dT}{dv}$, thus obtained, refers to the case of an isentropic variation, and hence we must write:

$$\frac{d_s T}{dv} = -\frac{T}{C_v} \times \frac{d_v p}{dT} \text{..................(10).}$$

Similarly we obtain from equation (4),

$$\frac{d_s T}{dp} = \frac{T}{C_p} \times \frac{d_p v}{dT} \text{..................(11).}$$

Applying either equation (5) or equation (7), we have

$$0 = C_p \frac{d_v p}{dT} dv + C_v \frac{d_p v}{dT} dp;$$

whence
$$\frac{d_s v}{dp} = -\frac{C_v}{C_p}\,\frac{\dfrac{d_p v}{dT}}{\dfrac{d_v p}{dT}}.$$

Applying equations (1) (2), this equation becomes

$$\frac{d_s v}{dp} = \frac{C_v}{C_p} \times \frac{d_T v}{dp} \quad \text{..................(12).}$$

If here we give to C_v its value from (7a), we obtain

$$\frac{d_s v}{dp} = \frac{d_T v}{dp} + \frac{T}{C_p}\left(\frac{d_p v}{dT}\right)^2 \quad \text{...............(13).}$$

If we take the reciprocal of (12), we obtain the equation

$$\frac{d_s p}{dv} = \frac{C_p}{C_v} \times \frac{d_T p}{dv} \quad \text{..................(14).}$$

This equation, if transformed in the same way as (12), gives

$$\frac{d_s p}{dv} = \frac{d_T p}{dv} - \frac{T}{C_v}\left(\frac{d_v p}{dT}\right)^2 \quad \text{...............(15).}$$

These differential coefficients between volume and pressure, for the case of the entropy being constant, have been applied to calculate the velocity of propagation of sound in gases and liquids, as has been already described in Chapter II. for the case of perfect gases.

§ 8. *Special Forms of the Fundamental Equations for an Expanded Rod.*

Hitherto we have always considered the external force to be a uniform surface pressure. We will now give an example of a different kind of force, and will take the case of an elastic rod or bar, which is extended lengthwise by a tensional strain, e.g. a hanging weight, whilst no forces act upon it in a transverse direction. Instead of a tensional we may take a compressive strain, so long as the rod is not thereby bent. This we should simply treat in the formulae as a negative tension. The condition that no transverse force acts on the rod would be exactly fulfilled only if the rod were placed in vacuo and thus freed from the atmospheric pressure. But, since the longitudinal strain, which acts on the cross section, is very large in comparison with the atmospheric pressure upon an equal area, the latter may be neglected.

Let P be the force, and l the length of the rod, when acted on by the force and at temperature T. The length, and in general the whole condition, of the rod is under these conditions determined by the quantities P and T; and we may therefore choose these as independent variables.

Let us now suppose that by an indefinitely small change in the force or temperature or both, the length l is increased by dl. The work Pdl will then have been done by the force P. Since however in our formulae we have taken as positive not the work done but the work destroyed by a force, the equation for determining the external work must be written

$$dW = -Pdl \text{ ....(16).}$$

Taking l as a function of P and T, we may write this equation as follows:

$$dW = -P\left(\frac{dl}{dP}dP + \frac{dl}{dT}dT\right);$$

whence $$\frac{dW}{dP} = -P\frac{dl}{dP}; \quad \frac{dW}{dT} = -P\frac{dl}{dT}.$$

Differentiating the first of these equations according to T and the second according to P, and observing that, since P and T are independent variables, $\frac{dP}{dT} = 0$, we have

$$\frac{d}{dT}\left(\frac{dW}{dP}\right) = -P\frac{d^2l}{dPdT},$$

$$\frac{d}{dP}\left(\frac{dW}{dT}\right) = -\frac{dl}{dT} - P\frac{d^2l}{dTdP}.$$

If we subtract the second of these from the first, and substitute for the difference on the left-hand side of the resulting equation the symbol already employed for the same purpose, viz. D_{PT}, we have

$$D_{PT} = \frac{dl}{dT} \text{ ....(17).}$$

This value of D_{PT} we will apply to equations (12), (13), (14), (15) of Chapter V., substituting P for x in this particular case throughout. We then obtain the fundamental equations, in the following form:

$$\frac{d}{dT}\left(\frac{dQ}{dP}\right) - \frac{d}{dP}\left(\frac{dQ}{dT}\right) = \frac{dl}{dT} \quad \text{.............(18)},$$

$$\frac{d}{dT}\left(\frac{dQ}{dP}\right) - \frac{d}{dP}\left(\frac{dQ}{dT}\right) = \frac{1}{T}\frac{dQ}{dT} \quad \text{..........(19)},$$

$$\frac{dQ}{dT} = T\frac{dl}{dT} \quad \text{....................(20)},$$

$$\frac{d}{dP}\left(\frac{dQ}{dT}\right) = T\frac{d^2l}{dT^2} \quad \text{...............(21)}.$$

§ 9. *Alteration of Temperature during the extension of the Rod.*

The form of equation (20) indicates a special relation between two processes, viz. the alteration in temperature produced by an alteration in length, and the alteration in length produced by an alteration in temperature. Thus if, as is usually the case, the rod lengthens when heated under a constant strain, and $\frac{dl}{dT}$ is therefore positive, the equation shews that $\frac{dQ}{dT}$ is also positive; whence it follows that, if the rod is lengthened by an increase in the external force, it must take in heat from without if it is to keep its temperature constant, or in other words, if no heat is imparted to it, it will cool during extension. On the other hand if, as may happen in exceptional cases, the rod shortens when heated at constant pressure, and therefore $\frac{dl}{dT}$ is negative, then the equation shews that $\frac{dQ}{dT}$ is also negative. In this case the rod must give out heat, when lengthened by an increase of strain, if it is to preserve a constant temperature; and if no giving out of heat takes place it must grow warmer in lengthening.

The magnitude of the alteration of temperature which takes place if the force is varied, without any heat being imparted to or taken from the rod, is easily determined if we form the complete differential equation of the first order for Q, in the same way as we have already done in the case of bodies under a uniform surface pressure. The differential coefficient $\frac{d_TQ}{dP}$ is determined by equation (20), in which we will write for $\frac{dl}{dT}$ the fuller form $\frac{d_Pl}{dT}$. In order to express the other differential coefficient $\frac{d_PQ}{dT}$ in a convenient form, we may denote the specific heat of the rod under constant strain by C_P, and the weight of the rod by M. Then we have

$$\frac{d_PQ}{dT} = MC_P,$$

and the complete differential equation is as follows:

$$dQ = MC_PdT + T\frac{d_Pl}{dT} \quad\text{..................(22)}.$$

If we now assume that no heat is imparted to or taken from the rod, we must put $dQ = 0$, which gives

$$0 = MC_PdT + T\frac{d_Pl}{dT}dP.$$

If we divide this equation by dP, the quotient $\frac{dT}{dP}$ expresses that differential coefficient of T according to P, in the formation of which the entropy is taken as constant; it should therefore be written more fully $\frac{d_ST}{dP}$. We thus obtain the following equation:

$$\frac{d_ST}{dP} = -\frac{T}{MC_P} \times \frac{d_Pl}{dT} \quad\text{.................. (23)}.$$

This equation was first developed, though in a slightly different form, by Sir William Thomson, and its correctness was experimentally verified by Joule*. The agreement of observation and theory was specially brought out by a phenomenon occurring with India rubber, which had already been noticed by Gough, but was then observed also by Joule and verified by accurate measurements. So long as India rubber is not extended at all, or only by a very small force, it behaves, with regard to alterations in length produced by alterations in temperature, in the same way as other bodies; i.e. it lengthens when heated and shortens when cooled. When however it is extended by a greater force its behaviour is the opposite; i.e. it shortens when heated and lengthens when cooled. The differential coefficient $\frac{d_pl}{dT}$ is thus positive in the first case and negative in the second. In accordance with this it exhibits the peculiarity that it is cooled by an increase of the strain, so long as the strain remains small, but is heated by an increase of the strain when the strain is large. This agrees with equation (23), according to which $\frac{d_sT}{dP}$ must always have the opposite sign to $\frac{d_pl}{dT}$.

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* *Phil. Trans.*, 1859.

§ 10. *Further Deductions from the Equations.*

The complete differential equation (22) may also be so formed as to present T and l, or l and P, as the independent variables. For this purpose we must first state the relation which holds between the differential coefficients of the quantities T, l, and P. This relation will be expressed by an equation of the same form as (2), viz.:

$$\frac{d_TP}{dl} \times \frac{d_pl}{dT} \times \frac{d_lT}{dP} = -1 \text{ .... } (24).$$

First, to form the complete differential equation which contains T and l as independent variables, we must consider P as a function of T and l, and accordingly write (22) in the form

$$dQ = MC_pdT + T\frac{d_pl}{dT}\left(\frac{d_lP}{dT}dT + \frac{d_TP}{dT}dl\right)$$

$$= \left(MC_p + T\frac{d_pl}{dT}\frac{d_lP}{dT}\right)dT + T\frac{d_pl}{dT}\frac{d_TP}{dl}dl.$$

Transforming the last term by means of equation (24), we have

$$dQ = \left(MC_p + T\frac{d_p l}{dT} \times \frac{d_l P}{dT}\right) dT - T\frac{d_l P}{dT}\, dl \ldots\ldots (25).$$

If we denote by C_l the specific heat at constant length, the coefficient of dT in this equation must be equal to MC_l; whence

$$C_l = C_p + \frac{T}{M} \times \frac{d_p l}{dT} \times \frac{d_l P}{dT} \ldots\ldots\ldots\ldots\ldots\ldots (26).$$

Transforming this by means of (24), we have

$$C_l = C_p - \frac{T}{M} \times \frac{\left(\frac{d_p l}{dT}\right)^2}{\frac{d_T l}{dP}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (27).$$

Equation (25) assumes then the following simplified form:

$$dQ = MC_l dT - T\frac{d_l P}{dT}\, dl \ldots\ldots\ldots\ldots\ldots (28).$$

Secondly, to form the complete differential equation which contains l and P as independent variables, we must consider T as a function of l and P. Equation (22) then becomes

$$dQ = MC_p\left(\frac{d_p T}{dl} + \frac{d_l T}{dP}\, dP\right) + T\frac{d_p l}{dT} dP$$

$$= MC_p\frac{d_p T}{dl}\, dl + \left(MC_p\frac{d_l T}{dP} + T\frac{d_p l}{dT}\right) dP.$$

Transforming the coefficient of dP, we have

$$dQ = MC_p\frac{d_p T}{dl}\, dl + \left(MC_p + T\frac{d_p l}{dT} \times \frac{d_l P}{dT}\right)\frac{d_l T}{dP}\, dP.$$

By equation (26) MC_l can be substituted for the expression in brackets. The equation then becomes

$$dQ = MC_p\frac{d_p T}{dl}\, dl + MC_l\frac{d_l T}{dP}\, dP \ldots\ldots\ldots (29).$$

We will again apply equations (28) and (29) to the case of the rod when it neither receives nor gives out any heat, and therefore $dQ=0$. The first equation then becomes

$$\frac{d_sT}{dl}=\frac{T}{MC_l}\times\frac{d_lP}{dT}\;\ldots\ldots\ldots\ldots\ldots\ldots\ldots(30);$$

and the second

$$\frac{d_sl}{dP}=-\frac{C_l}{C_p}\times\frac{\dfrac{d_lT}{dP}}{\dfrac{d_pT}{dl}}.$$

But by equation (24) we may write the latter thus:

$$\frac{d_sl}{dP}=\frac{C_l}{C_p}\times\frac{d_Tl}{dP}\;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(31).$$

Giving to C_l its value according to (27), we have

$$\frac{d_sl}{dP}=\frac{d_Tl}{dP}-\frac{T}{MC_p}\left(\frac{d_pl}{dT}\right)^2\;\ldots\ldots\ldots\ldots\ldots(32).$$

The relation between length and stretching force which is expressed by the differential coefficient $\frac{d_sl}{dP}$, as here determined, is that which has to be applied to calculate the velocity of sound in an elastic rod, in place of the relation expressed by the differential coefficient $\frac{d_Tl}{dP}$, which is commonly used, and which is determined by the coefficient of elasticity. In the same way, to calculate the velocity of sound in gaseous and liquid bodies, we must use the relation between volume and pressure expressed by $\frac{d_sv}{dp}$ in place of that expressed by $\frac{d_Tv}{dp}$. We may however remark that in treating of the propagation of sound, in cases where the force P is not large, we may in equation (32), which serves to determine $\frac{d_sl}{dp}$, substitute for the specific heat at constant tension, denoted by C_p, the specific heat at constant pressure, as measured in the ordinary way under the pressure of the atmosphere.

CHAPTER IX.

DETERMINATION OF ENERGY AND ENTROPY.

§ 1. *General Equations.*

In former chapters we have repeatedly spoken of the Energy and Entropy of a body as being two magnitudes of great importance in the Science of Heat, which are determined by the condition of the body at the moment, without its being necessary to know the way in which the body has come into this condition. Knowing these magnitudes, we can easily make by their aid various calculations relating to the body's changes in condition, and the quantity of heat thereby brought into action. One of these, the Energy, has already been made the subject of many valuable researches, especially by Kirchhoff[*], and the method of determining it is therefore more accurately known. We will here treat of Energy and Entropy simultaneously, and set forth side by side the equations which serve to determine them.

In Chapters I. and III. the two following fundamental equations, denoted by (III.) and (VI.) were developed:

$$dQ = dU + dW \text{.....................(III)},$$

$$dQ = TdS \text{...........................(VI)}.$$

Here U and S denote the Energy and Entropy of the body, and dU and dS the changes produced in them by an indefinitely small change in the body's condition: dQ is the quantity of heat taken in by the body during its change;

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[*] Pogg. *Ann.*, Vol. CIII. p. 177.

dW the external work performed; and T the absolute temperature at which the change takes place. The first equation is applicable to any indefinitely small change of condition, in whatever way it takes place, but the latter can be applied only to such changes as are in their nature reversible. These two equations we will now write in the form:

$$dU = dQ - dW \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)},$$

$$dS = \frac{dQ}{T} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}.$$

Their integration will then determine U and S.

Here we must first notice a point which has already been mentioned with regard to energy in Chapter I., § 8. It is not possible to determine the whole energy of a body, but only the increase which the energy has received, whilst the body was passing into its present condition from some other which we choose as its initial condition; and the same is also true of the Entropy.

Now to apply equation (1). Let us suppose that the body has been brought into its present condition from the given initial condition, the energy of which we will denote by U_0, by any convenient path, and in any way reversible or not reversible; and let us suppose dU to be integrated through the range of this change in condition. The value of this integral will be simply $U - U_0$. The integrals of dQ and dW represent the whole quantity of heat which the body has taken in, and the whole external work which it has performed, during the change in condition. These we will denote by Q and W. Then we have the equation

$$U = U_0 + Q - W \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}.$$

Hence it follows that if for any mode of passing from a given initial condition to the present condition of the body, we can determine the heat taken in and the work performed, we thereby know also the energy of the body, except as regards one constant depending on the initial condition.

Next to apply equation (2). Let us suppose that the body has been brought into its present condition from the given initial condition, the entropy of which we denote by S_0, by any path whatever, but by a process which is reversible;

and let us suppose the equation integrated for this change in condition. The integral of dS will have the value $S - S_0$: whence we have

$$S = S_0 + \int \frac{dQ}{T} \quad \text{.....................(4).}$$

Hence it follows that if for any passage of the body, by a reversible method but by any path whatever, from a given initial condition to its present condition, we can determine $\int \frac{dQ}{T}$, we shall thereby know the value of the entropy, except as regards one constant depending on the initial condition.

§ 2. *Differential Equations for the Case in which only Reversible Changes take place, and in which the condition of the Body is determined by two Independent Variables.*

If we apply both the equations (III.) and (VI.) to one and the same indefinitely small and reversible change in the body's condition, the element dQ will be the same in both equations, and may therefore be eliminated. Hence we have

$$TdS = dU + dW \quad \text{.....................(5).}$$

We will now assume that the condition of the body is determined by two variables, which, as in Chapter VI., we will generally denote by x and y, signifying by these certain magnitudes to be fixed later on, such as temperature, volume, pressure. If the condition is determined by x and y, then all magnitudes, the values of which are fixed by the condition of the body at the moment, without its being necessary to know the way in which the body has come into that condition, are capable of being represented by functions of these variables; in which functions the variables must be considered as independent of each other. Accordingly the entropy S and the energy U must be looked upon as functions of x and y. On the other hand, the external work W, as we have repeatedly observed, holds a completely different position in this relation. It is true that the differential coefficients of W, so far as concerns reversible changes, may be considered as known functions of x and y: W itself however cannot be represented by such a function, and can only be determined, if we have given not only the initial and final conditions of the body, but also the path by which it has passed from one to the other.

If in equation (5) we put

$$dS = \frac{dS}{dx}dx + \frac{dS}{dy}dy,$$

$$dU = \frac{dU}{dx}dx + \frac{dU}{dy}dy,$$

$$dW = \frac{dW}{dx}dx + \frac{dW}{dy}dy,$$

that equation becomes

$$T\frac{dS}{dx}dx + T\frac{dS}{dy}dy = \left(\frac{dU}{dx} + \frac{dW}{dx}\right)dx + \left(\frac{dU}{dy} + \frac{dW}{dy}\right)dy.$$

As this equation must hold for any values whatever of dx and dy, it must hold for the cases amongst others in which one or other of these differentials is equal to zero. Hence it divides into the two following equations:

$$\left.\begin{aligned} T\frac{dS}{dx} &= \frac{dU}{dx} + \frac{dW}{dx} \\ T\frac{dS}{dy} &= \frac{dU}{dy} + \frac{dW}{dy} \end{aligned}\right\} \text{......................(6).}$$

From these equations either S or U may be eliminated by a second differentiation. We will first take U, as this gives rise to the simplest equation. For this purpose we must differentiate the first of equations (6) according to y, and the second according to x. We shall write the second differential coefficients of S and U in the ordinary manner: but the differential coefficients of $\frac{dW}{dx}$ and $\frac{dW}{dy}$ we will write as follows: $\frac{d}{dy}\left(\frac{dW}{dx}\right)$ and $\frac{d}{dx}\left(\frac{dW}{dy}\right)$. This is with the same object as in Chapter V., viz. to shew that they are not second differential coefficients of a function of x and y. Finally we may observe that T, the absolute temperature of the body, which in this investigation we assume to be uniform throughout the body, may also be considered as a function of x and y. We thus obtain

$$\frac{dT}{dy} \times \frac{dS}{dx} + T\frac{d^2S}{dx\,dy} = \frac{d^2U}{dx\,dy} + \frac{d}{dy}\left(\frac{dW}{dx}\right),$$

$$\frac{dT}{dx} \times \frac{dS}{dy} + T\frac{d^2S}{dy\,dx} = \frac{d^2U}{dy\,dx} + \frac{d}{dx}\left(\frac{dW}{dy}\right).$$

Subtracting the second of these equations from the first, and remembering that

$$\frac{d^2S}{dx\,dy} = \frac{d^2S}{dy\,dx}, \text{ and } \frac{d^2U}{dx\,dy} = \frac{d^2U}{dy\,dx},$$

we have

$$\frac{dT}{dy} \times \frac{dS}{dx} - \frac{dT}{dx} \times \frac{dS}{dy} = \frac{d}{dy}\left(\frac{dW}{dx}\right) - \frac{d}{dx}\left(\frac{dW}{dy}\right).$$

The right-hand side of this equation we have named in Chapter V., "the work difference referred to xy," and have denoted it by D_{xy}; hence we may put

$$D_{xy} = \frac{d}{dy}\left(\frac{dW}{dx}\right) - \frac{d}{dx}\left(\frac{dW}{dy}\right) \text{ ....(7);}$$

and the previous equation becomes

$$\frac{dT}{dy} \times \frac{dS}{dx} - \frac{dT}{dx} \times \frac{dS}{dy} = D_{xy} \text{ ....(8).}$$

This is the differential equation, derived from equation (5), which serves to determine (S).

Secondly, to eliminate S from equations (6), we write them in the following form :

$$\frac{dS}{dx} = \frac{1}{T}\frac{dU}{dx} + \frac{1}{T}\frac{dW}{dx},$$

$$\frac{dS}{dy} = \frac{1}{T}\frac{dU}{dy} + \frac{1}{T}\frac{dW}{dy}.$$

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Differentiating the first of these equations according to y, and the second according to x, we have

$$\frac{d^2S}{dxdy}=\frac{1}{T}\times\frac{d^2U}{dxdy}-\frac{1}{T^2}\times\frac{dT}{dy}\times\frac{dU}{dx}+\frac{d}{dy}\left(\frac{1}{T}\frac{dW}{dx}\right),$$

$$\frac{d^2S}{dy\,dx}=\frac{1}{T}\times\frac{d^2U}{dydx}-\frac{1}{T^2}\times\frac{dT}{dx}\times\frac{dU}{dy}+\frac{d}{dx}\left(\frac{1}{T}\frac{dW}{dy}\right).$$

Subtracting the second of these equations from the first, putting all the terms containing U in the resulting equation on the left-hand side, and multiplying the whole equation by T^2, we have

$$\frac{dT}{dy}\times\frac{dU}{dx}-\frac{dT}{dx}\times\frac{dU}{dy}=T^2\left[\frac{d}{dy}\left(\frac{1}{T}\frac{dW}{dx}\right)-\frac{d}{dx}\left(\frac{1}{T}\frac{dW}{dy}\right)\right].$$

We will adopt a special symbol for the right-hand side of this equation, viz.,

$$\Delta_{xy}=T^2\left[\frac{d}{dy}\left(\frac{1}{T}\frac{dW}{dx}\right)-\frac{d}{dx}\left(\frac{1}{T}\frac{dW}{dy}\right)\right]\text{.........}(9);$$

and we may point out that between D_{xy} and Δ_{xy} there is the following relation:

$$\Delta_{xy}=TD_{xy}-\frac{dT}{dy}\frac{dW}{dx}+\frac{dT}{dx}\frac{dW}{dy}\text{ ....}(10).$$

Using this symbol, the above equation assumes the form

$$\frac{dT}{dy}\frac{dU}{dx}-\frac{dT}{dx}\frac{dU}{dy}=\Delta_{xy}\text{ ....}(11).$$

This is the differential equation, derived from equation (5), which serves to determine U.

§ 3. *Introduction of the Temperature as one of the Independent Variables.*

The above equations take a specially simple form, if the temperature T is chosen as one of the independent variables. If we put $T=y$, we have

$$\frac{dT}{dy}=1,\ \frac{dT}{dx}=0.$$

We thus obtain from (10) the following expression of the relation between Δ_{xy} and D_{xy}:

$$\Delta_{xT} = TD_{xT} - \frac{dW}{dx} \quad \ldots\ldots\ldots\ldots\ldots\ldots(12).$$

Equations (8) and (11) also become

$$\left.\begin{aligned} \frac{dS}{dx} &= D_{xT} \\ \frac{dU}{dx} &= \Delta_{xT} \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13).$$

The differential coefficients of the two functions S and U with regard to x are thus known. For their differential coefficients with respect to T we will take the expressions which follow directly from (2) and (1) on the assumption that the condition of the body is determined by T and x, viz.:

$$\left.\begin{aligned} \frac{dS}{dT} &= \frac{1}{T}\frac{dQ}{dT}, \\ \frac{dU}{dT} &= \frac{dQ}{dT} - \frac{dW}{dT} \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots(14).$$

From equations (13) and (14) we can form the following complete differential equations:

$$\left.\begin{aligned} dS &= \frac{1}{T}\frac{dQ}{dT}\,dT + D_{xT}\,dx, \\ dU &= \left(\frac{dQ}{dT} - \frac{dW}{dT}\right)dT + \Delta_{xT}\,dx \end{aligned}\right\} \quad \ldots\ldots\ldots(15).$$

Since S and U must be capable of being expressed as functions of T and x, in which functions these two variables may be taken as independent of each other, the well-known condition of integrability must hold for the case of the two equations just given. For the first equation this condition is

$$\frac{d}{dx}\left(\frac{1}{T}\frac{dQ}{dT}\right) = \frac{dD_{xT}}{dT},$$

or

$$\frac{d}{dx}\left(\frac{dQ}{dT}\right) = T\frac{dD_{xT}}{dT} \quad \ldots\ldots\ldots\ldots\ldots\ldots(16),$$

which is equation (15) of Chapter V. For the second equation the condition is

$$\frac{d}{dx}\left(\frac{dQ}{dT}\right)-\frac{d}{dx}\left(\frac{dW}{dT}\right)=\frac{d\Delta_{xT}}{dT}\ \ldots\ldots\ldots\ldots(17).$$

This equation can be easily shewn to depend on the last. For by (12)

$$\Delta_{xT}=TD_{xT}-\frac{dW}{dx}.$$

Differentiating this equation according to T, we have

$$\frac{d\Delta_{xT}}{dT}=T\frac{dD_{xT}}{dT}+D_{xT}-\frac{d}{dT}\left(\frac{dW}{dx}\right).$$

Now, remembering that

$$D_{xT}=\frac{d}{dT}\left(\frac{dW}{dx}\right)-\frac{d}{dx}\left(\frac{dW}{dT}\right),$$

we may write this equation as follows:

$$\frac{d\Delta_{xT}}{dT}=T\frac{dD_{xT}}{dT}-\frac{d}{dx}\left(\frac{dW}{dT}\right).$$

On substituting this value of $\frac{d\Delta_{xT}}{dT}$ in equation (17), we are brought back to the form of equation (16).

We have now to determine S and U themselves, by integrating equations (15). Let us suppose that the body has been brought into its present condition, by any path we please, from an initial condition for which the quantities T, S, x, U have the values T_0, S_0, x_0, U_0 respectively: and let this particular change of condition give the range of the integration. As an example, let us suppose that the body is first heated from the temperature T_0 to the temperature T, while the other variable keeps its initial value x_0, and then that this other variable changes its value from x_0 to x, while the temperature remains constant. Then we have

$$\left.\begin{aligned} S &= S_0+\int_{T_0}^{T}\left(\frac{1}{T}\frac{dQ}{dT}\right)_{x=x_0}dT+\int_{x_0}^{x}D_{xT}dx,\\ U &= U_0+\int_{T_0}^{T}\left(\frac{dQ}{dT}-\frac{dW}{dT}\right)_{x=x_0}dT+\int_{x_0}^{x}\Delta_{xT}dx \end{aligned}\right\}(18).$$

In both these equations the first integral on the right-hand side is a simple function of T, whilst the second is a function of T and x.

Let us now make the opposite assumption, viz. that the change of x first takes place at the initial value of T, and then the change of T at the final value of x. Then we obtain

$$\left.\begin{aligned} S &= S_0 + \int_{x_0}^{x} (D_{xT})_{T=T_0}\, dx + \int_{T_0}^{T} \frac{1}{T} \times \frac{dQ}{dT}\, dT, \\ U &= U_0 + \int_{x_0}^{x} (\Delta_{xT})_{T=T_0}\, dx + \int_{T_0}^{T} \left(\frac{dQ}{dT} - \frac{dW}{dT}\right) dT \end{aligned}\right\} \text{......(19).}$$

In both these equations the first integral on the right-hand side is a simple function of x, and the second of T and x.

By what has been said above, we may choose any other path whatever, instead of that which we have taken as our example, in which path the changes of T and x may be transposed in any way, or may both take place at once according to any law. We should naturally in each special case choose that path, for which the data requisite to perform the calculation are most accurately known.

§ 4. *Special case of the Differential equations on the assumption that the only external force is a Uniform Surface Pressure.*

If we assume as the only External Force a Uniform Pressure normal to the surface, we must put

$$dW = p dv.$$

Hence
$$\frac{dW}{dx} = p\frac{dv}{dx} \text{ and } \frac{dW}{dy} = p\frac{dv}{dy}.$$

The expressions for D_{xy} and Δ_{xy} then assume peculiar forms. Those for D_{xy} have been already considered in Chapter V. We have first

$$D_{xy} = \frac{d}{dy}\left(p\frac{dv}{dx}\right) - \frac{d}{dx}\left(p\frac{dv}{dy}\right),$$

$$\Delta_{xy} = T^2\left[\frac{d}{dy}\left(\frac{p}{T} \times \frac{dv}{dx}\right) - \frac{d}{dx}\left(\frac{p}{T} \times \frac{dv}{dy}\right)\right].$$

In the last of these equations we will put for the sake of brevity:

$$\pi = \frac{p}{T} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (20),$$

whereby it becomes

$$\Delta_{xy} = T^2 \left[\frac{d}{dy}\left(\pi \frac{dv}{dx}\right) - \frac{d}{dx}\left(\pi \frac{dv}{dy}\right)\right].$$

Performing the differentiation in these equations, and remembering that $\frac{d^2v}{dxdy} = \frac{d^2v}{dydx}$, we have

$$D_{xy} = \frac{dp}{dy} \times \frac{dv}{dx} - \frac{dp}{dx} \times \frac{dv}{dy} \ldots\ldots\ldots\ldots (21).$$

$$\Delta_{xy} = T^2 \left(\frac{d\pi}{dy} \times \frac{dv}{dx} - \frac{d\pi}{dx} \times \frac{dv}{dy}\right) \ldots\ldots\ldots (22).$$

If the temperature T be selected as one independent variable, whilst the other remains x as before, the expressions become

$$D_{xT} = \frac{dp}{dT} \times \frac{dv}{dx} - \frac{dp}{dx} \times \frac{dv}{dT} \ldots\ldots\ldots\ldots (23),$$

$$\Delta_{xT} = T^2 \left(\frac{d\pi}{dT} \times \frac{dv}{dx} - \frac{d\pi}{dx} \times \frac{dv}{dT}\right) \ldots\ldots\ldots\ldots (24);$$

or, restoring to π its value $\frac{p}{T}$,

$$\Delta_{xT} = T\left(\frac{dp}{dT} \times \frac{dv}{dx} - \frac{dp}{dx} \times \frac{dv}{dT}\right) - p\frac{dv}{dx} \ldots\ldots (24a).$$

The equations (15) then assume the following forms:

$$dS = \frac{1}{T} \times \frac{dQ}{dT} dT + \left(\frac{dp}{dT} \times \frac{dv}{dx} - \frac{dp}{dx} \times \frac{dv}{dT}\right) dx \ldots\ldots\ldots\ldots (25),$$

$$dU = \left(\frac{dQ}{dT} - p\frac{dv}{dT}\right) dT + T^2 \left(\frac{d\pi}{dT} \times \frac{dv}{dx} - \frac{d\pi}{dx} \times \frac{dv}{dT}\right) dx \ldots (26);$$

or written in another form,

$$dU = \left(\frac{dQ}{dT} - p\frac{dv}{dT}\right)dT + \left[T\left(\frac{dp}{dT} \times \frac{dv}{dx} - \frac{dp}{dx} \times \frac{dv}{dT}\right) - p\frac{dv}{dx}\right] dx \;\ldots\ldots(26a).$$

If we further choose for the second variable, as yet undetermined, the volume v, and thus put $x = v$, we have

$$\frac{dv}{dx} = 1 \text{ and } \frac{dv}{dT} = 0.$$

Hence the preceding equations become

$$\left.\begin{aligned} dS &= \frac{1}{T}\frac{dQ}{dT}dT + \frac{dp}{dT}dv, \\ dU &= \frac{dQ}{dT}dT + \left(T\frac{dp}{dT} - p\right)d \end{aligned}\right\}\ldots\ldots\ldots\ldots(27).$$

If the pressure p be chosen as the second independent variable, so that $x = p$, we have

$$\frac{dp}{dx} = 1 \text{ and } \frac{dp}{dT} = 0\,;$$

and the equations become

$$\left.\begin{aligned} dS &= \frac{1}{T}\frac{dQ}{dT}dT - \frac{dv}{dT}dp, \\ dU &= \left(\frac{dQ}{dT} - p\frac{dv}{dT}\right)dT - \left(T\frac{dv}{dT} + p\frac{dv}{dp}\right)dp \end{aligned}\right\}\ldots\ldots(28).$$

§ 5. *Application of the foregoing Equations to Homogeneous Bodies, and in particular to Perfect Gases.*

For Homogeneous Bodies, where the only external force is a uniform pressure normal to the surface, it is usual, as at the end of the last section, to choose for independent variables two of the quantities T, v, p; and $\frac{dQ}{dT}$ then takes the simple significations which we have several times alluded to. Thus if T and v are the independent variables, and if the weight of the body be a unit of weight, $\frac{dQ}{dT}$ signifies the specific heat at constant volume: or, if T and p are the independent variables, the specific heat at constant pressure. Equations (27) and (28) become in these cases

$$\left.\begin{aligned} dS &= \frac{C_v}{T}\,dT + \frac{dp}{dT}\,dv, \\ dU &= C_v dT + \left(T\frac{dp}{dT} - p\right) dv \end{aligned}\right\} \text{.............(29)},$$

$$\left.\begin{aligned} dS &= \frac{C_p}{T}\,dT - \frac{dv}{dT}\,dp, \\ dU &= \left(C_p - p\frac{dv}{dT}\right) dT - \left(T\frac{dv}{dT} + p\frac{dv}{dp}\right) dp \end{aligned}\right\} \text{(30)}.$$

If we wish to apply these equations to a perfect gas, we may use the following well known equation:

$$pv = RT.$$

Hence, if T and v be selected as independent variables,

$$\frac{dp}{dT} = \frac{R}{v},$$

and equations (29) then become

$$\left.\begin{aligned} dS &= C_v\frac{dT}{T} + R\frac{dv}{v} \\ dU &= C_v dT \end{aligned}\right\} \text{..................(31)}.$$

As in this case C_v must be regarded as a constant, these equations can at once be integrated, and give

$$\left.\begin{aligned} S &= S_0 + C_v \log\frac{T}{T_0} + R\log\frac{v}{v_0} \\ U &= U_0 + C_v(T - T_0) \end{aligned}\right\} \text{.............(32)}.$$

If we choose T and p as independent variables, we may put

$$\frac{dv}{dT} = \frac{R}{p} \text{ and } \frac{dv}{dp} = -\frac{RT}{p^2};$$

accordingly equations (30) become

$$\left.\begin{aligned} dS &= C_p \frac{dT}{T} - R\frac{dp}{p} \\ dU &= (C_p - R)\, dT \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots(33).$$

Whence we obtain by integration

$$\left.\begin{aligned} S &= S_0 + C_p \log\frac{T}{T_0} - R\log\frac{p}{p_0} \\ U &= U_0 + (C_p - R)(T - T_0) \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots(34).$$

The integration of the general equations (29) and (30) can of course only be accomplished if, in (29), p and C_v are known functions of T and v, or if, in (30), v and C_p are known functions of T and p.

§ 6. *Application of the Equations to a Body composed of matter in two Different States of Aggregation.*

As another special case we may select the state of things treated of in Chapters VI. and VII., viz. the case in which the body under consideration is partly in one state of aggregation and partly in another, and when the change, which the body may undergo at constant temperature, is such that the magnitudes of the parts in the two different states of aggregation are altered, with a corresponding change in the volume, but no change in the pressure. In this case the pressure p depends only on the temperature; and we may therefore put $\frac{dp}{dx} = 0$, by which equations (25) and (26) are transformed as follows:

$$\left.\begin{aligned} dS &= \frac{1}{T} \times \frac{dQ}{dT}\, dT + \frac{dp}{dT} \times \frac{dv}{dx}\, dx, \\ dU &= \left(\frac{dQ}{dT} - p\frac{dv}{dT}\right) dT + \left(T\frac{dp}{dT} - p\right)\frac{dv}{dx}\, dx \end{aligned}\right\} \quad (35).$$

As in Chapters VI. and VII., let us denote by M the weight of the whole mass, and by m the weight of the part in the second state of aggregation; and let us take m in place of x

for the second independent variable; then equation (6), Chapter VI., becomes

$$\frac{dv}{dm} = u,$$

for which, by equation (12), Chapter VI., we may substitute

$$\frac{dv}{dm} = \frac{\rho}{T\dfrac{dp}{dT}}.$$

Then the above equations become

$$\left.\begin{aligned} dS &= \frac{1}{T}\frac{dQ}{dT}dT + \frac{\rho}{T}dm, \\ dU &= \left(\frac{dQ}{dT} - p\frac{dv}{dT}\right)dT + \rho\left(1 - \frac{p}{T\dfrac{dp}{dT}}\right)dm \end{aligned}\right\} \quad (36).$$

To integrate these equations we may take as a starting point the condition that the whole mass M is in the first state of aggregation, that its temperature is T_0, and that its pressure is the pressure corresponding to that temperature. The passage from this to its present condition (in which the temperature is T, and in which the part m of the whole mass is in the second, and the part $M-m$ in the first state of aggregation) may be supposed to take place in the following way:—First let the mass, still remaining entirely in the first state of aggregation, be heated from T_0 to T, and let the pressure change at the same time, in such a way that it is always the pressure corresponding to the temperature at the moment: then let the part m pass at temperature T from the first to the second state of aggregation. The integration has to be performed according to these two successive stages.

During the first stage $dm = 0$, and thus it is only the first term on the right-hand side which has to be integrated. Here $\frac{dQ}{dT}$ has the value MC, where C signifies the specific heat of the body in its first state of aggregation, and for the case in which the pressure changes during the heating in the way described above. This kind of specific heat has been already discussed several times, and the conclusions drawn in Chap. VIII., § 6, shew that where the first state of aggregation is the solid or liquid, and the second the gaseous, it may safely be taken, for purposes of numerical calculation, as equal to the specific heat at constant pressure. It is only at very high temperatures, for which the vapour tension increases very rapidly with the temperature, that the difference between the specific heat C and the specific heat at constant pressures is important enough to be taken into account. Further, during the first change the volume v has the value $M\sigma$, where σ is the specific volume of the substance in the first state of aggregation. During the second stage $dT=0$, and therefore it is only the second term on the right-hand side of equation (3*a*) which has to be integrated. This integration can be at once performed for both equations, since the coefficient of dm is a constant with regard to m. The resulting equations therefore are

$$\left.\begin{aligned} S &= S_0 + M\int_{T_0}^{T} \frac{C}{T}\,dT + \frac{m\rho}{T}, \\ U &= U_0 + M\int_{T_0}^{T}\left(C - p\,\frac{d\sigma}{dT}\right)dT + m\rho\left(1 - \frac{p}{T\dfrac{dp}{dT}}\right) \end{aligned}\right\}\ldots(37).$$

If in these equations we put $m=0$ or $m=M$, we obtain the entropy and energy for the two cases in which the mass is either entirely in the first or entirely in the second state of aggregation, under the temperature T, and under the pressure corresponding to that temperature. For example, if the first state is the liquid and the second the gaseous, then if we put $m=0$, the expressions relate to the case of liquid under temperature T, and under a pressure equal to the maximum vapour tension at that temperature; or if we put $m=M$, they relate to saturated vapour at temperature T.

§ 7. *Relations of the Expressions* D_{xy} *and* Δ_{xy}.

In concluding this chapter it is worth while to refer again to the expressions D_{xy} and Δ_{xy}, which by (7) and (9) have the following meanings:

$$D_{xy} = \frac{d}{dy}\left(\frac{dW}{dx}\right) - \frac{d}{dx}\left(\frac{dW}{dy}\right),$$

$$\Delta_{xy} = T^2\left[\frac{d}{dy}\left(\frac{1}{T}\frac{dW}{dx}\right) - \frac{d}{dx}\left(\frac{1}{T}\frac{dW}{dy}\right)\right].$$

These are both functions of x and y: but if to determine the condition of the body we choose instead of x and y any two other variables which we may call ξ and η, we may form corresponding expressions $D_{\xi\eta}$ and $\Delta_{\xi\eta}$ as follows:

$$\left.\begin{aligned} D_{\xi\eta} &= \frac{d}{d\eta}\left(\frac{dW}{d\xi}\right) - \frac{d}{d\xi}\left(\frac{dW}{d\eta}\right), \\ \Delta_{\xi\eta} &= T^2\left[\frac{d}{d\eta}\left(\frac{1}{T}\frac{dW}{d\xi}\right) - \frac{d}{d\xi}\left(\frac{1}{T}\frac{dW}{d\eta}\right)\right] \end{aligned}\right\} \ldots\ldots(38).$$

These are of course functions of ξ and η, as the former were of x and y. But if we compare one of them, e.g. that for $D_{\xi\eta}$, with the corresponding expresssion for D_{xy}, we find that these are not simply two expressions for one and the same magnitude referred to different variables, but are actually two different magnitudes. For this reason D_{xy} has not been called simply the work difference, but the work difference referred to xy, so that it may be distinguished from $D_{\xi\eta}$, the work difference referred to $\xi\eta$. The same holds true of Δ_{xy} and $\Delta_{\xi\eta}$.

The relation which exists between D_{xy} and $D_{\xi\eta}$ may be found as follows. The differential coefficients which occur in the expression for $D_{\xi\eta}$ in (38), may be derived by first forming the differential coefficients according to x and y, and then treating each of these as a function of ξ and η. Thus we have

$$\frac{dW}{d\xi} = \frac{dW}{dx} \times \frac{dx}{d\xi} + \frac{dW}{dy} \times \frac{dy}{d\xi},$$

$$\frac{dW}{d\eta} = \frac{dW}{dx} \times \frac{dx}{d\eta} + \frac{dW}{dy} \times \frac{dy}{d\eta}.$$

Differentiating the first of these equations according to η and the second according to ξ, and again applying the same artifice, we have

$$\frac{d}{d\eta}\left(\frac{dW}{d\xi}\right) = \left\{\begin{aligned} &\frac{d}{dx}\left(\frac{dW}{dx}\right)\frac{dx}{d\xi}\frac{dx}{d\eta} + \frac{d}{dy}\left(\frac{dW}{dx}\right)\frac{dx}{d\xi}\frac{dy}{d\eta} \\ &+ \frac{dW}{dx}\frac{d^2x}{d\xi d\eta} + \frac{d}{dx}\left(\frac{dW}{dy}\right)\frac{dx}{d\eta}\frac{dy}{d\xi} \\ &+ \frac{d}{dy}\left(\frac{dW}{dy}\right)\frac{dy}{d\xi}\frac{dy}{d\eta} + \frac{dW}{dy}\frac{d^2y}{d\xi d\eta}, \end{aligned}\right.$$

$$\frac{d}{d\xi}\left(\frac{dW}{d\eta}\right) = \left\{ \begin{aligned} &\frac{d}{dx}\left(\frac{dW}{dx}\right)\frac{dx}{d\xi}\frac{dx}{d\eta} + \frac{d}{dy}\left(\frac{dW}{dx}\right)\frac{dx}{d\eta}\frac{dy}{d\xi} \\ &+ \frac{dW}{dx}\frac{d^2x}{d\xi d\eta} + \frac{d}{dx}\left(\frac{dW}{dy}\right)\frac{dx}{d\xi}\frac{dy}{d\eta} \\ &+ \frac{d}{dy}\left(\frac{dW}{dy}\right)\frac{dy}{d\xi}\frac{dy}{d\eta} + \frac{dW}{dy}\frac{d^2y}{d\xi d\eta}. \end{aligned} \right.$$

If we subtract the second of these equations from the first, all the terms on the right-hand side disappear except four, which may be expressed as the product of two binomial terms in the following equation:

$$\frac{d}{d\eta}\left(\frac{dW}{d\xi}\right) - \frac{d}{d\xi}\left(\frac{dW}{d\eta}\right) = \left(\frac{dx}{d\xi} \times \frac{dy}{d\eta} - \frac{dx}{d\eta} \times \frac{dy}{d\xi}\right)\left[\frac{d}{dy}\left(\frac{dW}{dx}\right) - \frac{d}{dx}\left(\frac{dW}{dy}\right)\right].$$

Here the expression on the left side is $D_{\xi\eta}$, and the expression in the square bracket is D_{xy}. Hence we have finally

$$D_{\xi\eta} = \left(\frac{dx}{d\xi} \times \frac{dy}{d\eta} - \frac{dx}{d\eta} \times \frac{dy}{d\xi}\right) D_{xy} \dots\dots\dots\dots (39).$$

Similarly we may obtain

$$\Delta_{\xi\eta} = \left(\frac{dx}{d\xi} \times \frac{dy}{d\eta} - \frac{dx}{d\eta} \times \frac{dy}{d\xi}\right) \Delta_{xy} \dots\dots\dots (39a).$$

If we substitute one new variable only, e.g. if we keep the variable x, but replace y by η, we must put $x = \xi$ in the two last equations, whence $\frac{dx}{d\xi} = 1$ and $\frac{dx}{d\eta} = 0$. The equations then become

$$D_{x\eta} = \frac{dy}{d\eta} D_{xy} \text{ and } \Delta_{x\eta} = \frac{dy}{d\eta} \Delta_{xy} \dots\dots\dots (40).$$

If we retain the original variables, but change their order of sequence, the expressions simply take the opposite sign, as is seen at once on inspection of (7) and (9). Hence

$$D_{xy} = -D_{xy} \text{ and } \Delta_{yx} = -\Delta_{xy} \dots\dots\dots\dots (41).$$

CHAPTER X.

ON NON-REVERSIBLE PROCESSES.

§ 1. *Completion of the Mathematical Expression for the second main Principle.*

In the proof of the second main principle, and in the investigations connected therewith, it was throughout assumed that all the variations are such as to be reversible. We must now consider how far the results are altered, when the investigations embrace non-reversible processes.

Such processes occur in very different forms, although in their substance they are nearly related to each other. One case of this kind has already been mentioned in Chapter I., viz., that in which the force under which a body changes its condition, e.g. the force of expansion of a gas, does not meet with a resistance equal to itself, and therefore does not perform the whole amount of work which it might perform during the change in condition. Other cases of the kind are the generation of heat by friction and by the resistance of the air, and also the generation of heat by a galvanic current in overcoming the resistance of the wire. Lastly the direct passage of heat from a hot to a cold body, by conduction or radiation, falls into this class.

We will now return to the investigation by which it was proved in Chapter IV. that in a reversible process the sum of all the transformations must be equal to zero. For one kind of transformation, viz. the passage of heat between bodies of different temperatures, it was taken as a fundamental principle depending on the nature of heat, that the passage from a lower to a higher temperature, which represents negative transformation, cannot take place without compensation. On this rested the proof that the sum of all the transformations in a cyclical process could not be negative, because, if any negative transformation remained over at the end, it could always be reduced to the case of a passage from a lower to a higher temperature. It was finally shewn that the sum of the transformations could not be positive, because it would then only be necessary to perform the process in a reverse order, in order to make the sum a negative quantity.

Of this proof the first part, that which shews that the sum of the transformations cannot be negative, still holds without alteration in cases where non-reversible transformations occur in the process under consideration. But the argument which shews that the sum cannot be positive is obviously inapplicable if the process is a non-reversible one. In fact a direct consideration of the question shews that there may very well be a balance left over of positive transformations; since in many processes, e.g. the generation of heat by friction, and the passage of heat by conduction from a hot to a cold body, a positive transformation alone takes place, unaccompanied by any other change.

Thus, instead of the former principle, that the sum of all the transformations must be zero, we must lay down our principle as follows, in order to include non-reversible variations:—

The algebraic sum of all the transformations which occur in a cyclical process must always be positive, or in the limit equal to zero.

We may give the name of uncompensated transformations to such as at the end of a cyclical process remain over without anything to balance them; and we may then express our principle more briefly as follows:—

Uncompensated transformations must always be positive.

In order to obtain the mathematical expression for this extended principle we need only remember that the sum of all the transformations in a cyclical process is given by $-\int\frac{dQ}{T}$. Thus to express the general principle, we must write in place of equation V. in Chapter III.,

$$\int\frac{dQ}{T}\leqq 0 \text{..........................(IX).}$$

Equation (VI.), Chapter III., then becomes

$$dQ \leqq TdS \quad \text{(X.)}$$

§ 2. *Magnitude of the Uncompensated Transformation.*

In many cases the magnitude of the Uncompensated Transformation is obtained directly from the equivalence value of the transformations, as determined by the method of Chapter IV. If for example a quantity of heat Q is generated by any process such as friction, and this is finally imparted to a body of temperature T, the uncompensated transformation thus produced has the value $\frac{Q}{T}$. Again, if a quantity of heat Q has passed by conduction from a body of temperature T_1 to another of temperature T_2, then the uncompensated transformation is $Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$. If a body has passed through a non-reversible cyclical process, and we wish to determine the resulting uncompensated transformation, which we may call N, we have, by the principles explained in Chapter IV., the equation

$$N = -\int \frac{dQ}{T} \quad (1).$$

As however a cyclical process may be made up of several individual changes of condition in a given body, some of which may be reversible, others non-reversible, it is in many cases interesting to know how much any particular one of the latter has contributed towards making up the whole sum of uncompensated transformations. For this purpose we may suppose that after the change of condition which we wish to enquire into, the variable body is brought by any reversible process into its former condition. By this means we form a smaller cyclical process, in which equation (1) may be applied just as well as in the whole process. Thus if we know the quantities of heat which the body has taken in during this process, and the temperatures which appertain to them, the negative integral $-\int \frac{dQ}{T}$ gives the uncompensated transformations which have taken place. But as the return to the original condition, which has taken place in a reversible manner, can have contributed nothing to increase this sum, the expression above gives the uncompensated transformation which was sought, and which was caused by the given change in condition.

If we examine in this way all the parts of the whole process which are non-reversible, and thereby find the values of N_1, N_2 etc., which must all be individually positive, then the sum of these gives the magnitude N relating to the whole cyclical process, without requiring us to bring under review those parts of it which are known to be reversible.

§ 3. *Expansion of a Gas unaccompanied by External Work.*

It may be worth while to examine more closely those changes of condition, mentioned in § 1, which take place in a non-reversible manner because the resistances to be overcome are less than the forces at work; our object being to determine the amount of heat taken in during the process. As however there are a great number of different changes of this kind, which are produced in a great number of ways, we must confine ourselves to a few cases, which are either especially noteworthy on account of their simplicity, or have some special interest on other grounds.

The general equation for determining the quantity of heat which a body takes in, whilst it undergoes any given change of condition, reversible or non-reversible, is as follows:

$$Q = U_2 - U_1 + W \qquad \text{.....................(2);}$$

in which U_1 and U_2 are the energy in the initial and final conditions, and W is the external work done during the variation.

To determine the energy we can employ the equations of Chapter IX. If the only external force is a uniform pressure, and if the condition of the body is determined by its temperature and volume, then we may use equation (29), viz.

$$dU = C_v\, dT + \left(T\frac{dp}{dT} - p\right) dv \qquad \text{...............(3).}$$

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This must be integrated for a passage in some reversible manner from the initial to the final condition. If the temperature is equal in the two conditions, as we shall assume in the examples which follow, then the integration may be performed at constant temperature, and the result will be, if we denote the initial and final volumes by v_1 and v_2,

$$U_2 - U_1 = \int_{v_1}^{v_2} \left(T \frac{dp}{dT} - p \right) dv \ldots\ldots\ldots\ldots\ldots (4);$$

whence equation (2) becomes

$$Q = \int_{v_1}^{v_2} \left(T \frac{dp}{dT} - p \right) dv + W \ldots\ldots\ldots\ldots (5).$$

As the first and simplest case we may take that in which a gas expands without doing any external work. We may suppose a quantity of the gas to be contained in a vessel and that this vessel is put in connection with another in which is a vacuum, so that part of the gas can pass from one to the other without meeting any external resistance. The quantity of heat which the gas must in this case take in, in order to keep its temperature unaltered, is determined by putting $W = 0$ in the last equation; thus we have

$$Q = \int_{v_1}^{v_2} \left(T \frac{dp}{dT} - p \right) dv \ldots\ldots\ldots\ldots\ldots\ldots (6).$$

If we make the special assumption that the gas is a perfect one, and therefore that $pv = RT$, we have

$$\frac{dp}{dT} = \frac{R}{v},$$

whence

$$T \frac{dp}{dT} = T \frac{R}{v} = \frac{pv}{R} \times \frac{R}{v} = p;$$

whence (6) becomes

$$Q = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7).$$

As already mentioned, Gay-Lussac, Joule, and Regnault have experimented on expansion apart from external work. Joule annexed to his experiments, described in Chapter II., by which he determined the heat generated in the compression

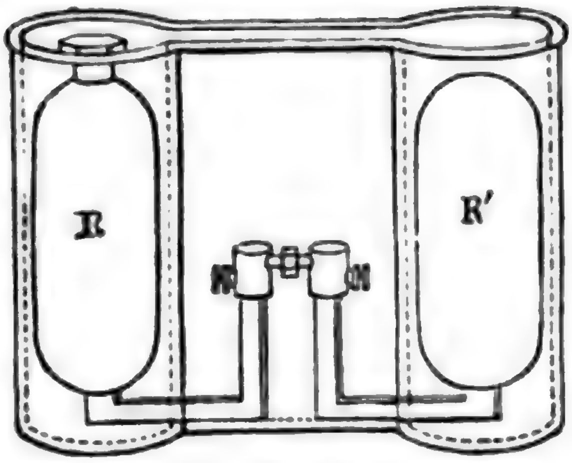

Fig. 18.

of air, other experiments upon the expansion of air. The receiver. *R*, shewn in Fig. 6, was filled with air condensed to 22 atmospheres, and was then connected, in the manner shewn in Fig. 18, with an empty receiver *R′*, so that the communication between the two was only closed by the cock. The two receivers were placed together in a water calorimeter, and the cock was then opened, whereupon the air passing over to the receiver *R′* expanded to about twice its former volume. The calorimeter shewed no loss of heat, and thus, so far as could be measured by this apparatus, no heat seemed to be required for the expansion of the air.

The above result however holds only for the process as a whole, and not for its individual parts. In the first receiver, in which the expansion takes place and the motion originates, heat is required; in the second, on the contrary, in which the motion ceases, and the air which rushes in first is compressed by that which follows, heat is generated; and so also in the places where friction has to be overcome during the passage. Since however the heat generated and the heat required are equal, they cancel each other; and we may say, so far as the general result of the whole process is concerned, that no expenditure of heat takes place.

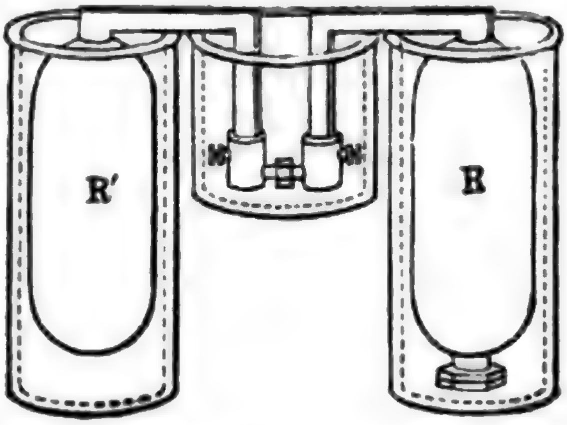

Fig. 19.

To observe specially the different parts of the process, Joule varied his experiment by placing the two receivers and the pipe carrying the cock in three different calorimeters, as shewn in Fig. 19. Then the calorimeter in which was the receiver containing the air shewed a loss of heat, and the two other calorimeters a gain. The whole gain and the whole loss were so nearly equal that Joule considers the difference to be within the limits of error of the observation.

§ 4. *Expansion of a Gas doing Partial Work.*

If a gas in expanding has a resistance to overcome, but one which is less than its expansive force, then an amount of work will be performed less than the amount which the gas could perform during the expansion. An example of this is the case of a gas rushing into the atmosphere out of a vessel in which it has a pressure higher than atmospheric pressure.

In this case also the process is a complicated one. We have not only to deal with the work necessary for the expansion and the corresponding consumption of heat, but in addition heat is consumed in producing the velocity with which the gas escapes; and heat is again generated when this velocity is subsequently checked. Similarly, heat is consumed in overcoming the resistance of friction, and is generated by the friction itself. To investigate accurately all these individual parts of the process would involve us in great difficulties.

If however we only wish to determine the quantity of heat, which on the whole must be taken in from without in order to keep the temperature of the gas constant, the case is simple. We can then leave out of account those parts of the process which balance each other, and need only consider the initial and final volume of the gas, and so much of the work done as is not transformed back again into heat. Then the internal work is the same as in any other case of the gas expanding at the same temperature and between the same initial and final volumes; while the external work is simply represented by the product of the increase of volume and the atmospheric pressure.

To determine the required quantity of heat, we start again from equation (5), and there substitute for W the expression for the external work performed in the present case, viz. $p_2(v_2 - v_1)$, where p_2 is the atmospheric pressure.

The equation thus becomes

$$Q = \int_{v_1}^{v_2} \left(T\frac{dp}{dT} - p \right) dv + p_2 (v_2 - v_1) \ldots \ldots\ldots\ldots (8).$$

If the gas is a perfect one, the integral on the right-hand side, as shewn in the last section, will = 0, and the equation takes the simpler form

$$Q = p_2 (v_2 - v_1) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9),$$

which expresses that in this case the heat taken in is only that corresponding to the work required for overcoming the external pressure of the air.

If the heat is to be measured according to the ordinary, not the mechanical unit, we must divide the right-hand side of (8) and (9) by the mechanical equivalent of heat, whence we have

$$Q = \frac{1}{E} \int_{v_1}^{v_2} \left(T\frac{dp}{dT} - p \right) dv + \frac{p_2}{E} (v_2 - v_1) \ldots\ldots (8a),$$

$$Q = \frac{p_2}{E} (v_2 - v_1) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9a).$$

This kind of expansion has also been experimented on by Joule. Having as before compressed air to a high pressure in a receiver, he allowed it to escape under atmospheric pressure. In order to bring the escaping air back to the original temperature, he caused it, after leaving the receiver, to pass through a long coil of pipe, as shewn in Fig. 20, which was placed together with the receiver in a water calorimeter. There then remained in the air only a small reduction of temperature, which it shared in common with the whole mass of the calorimeter. The cooling of the calorimeter gave the quantity of heat given off to the air during

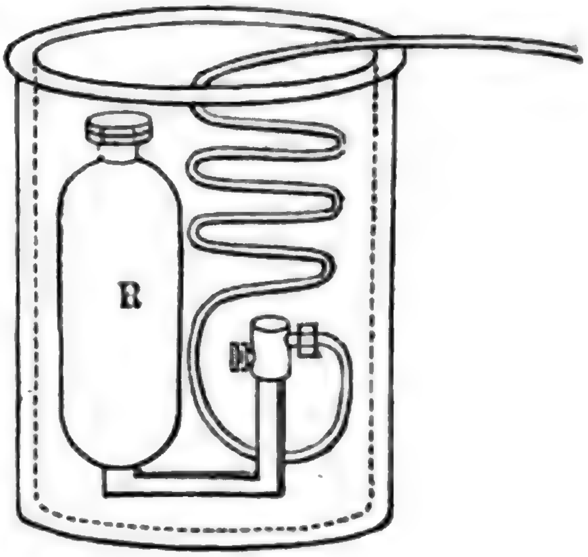

Fig. 20.

its expansion. Applying equation (9*a*) to this quantity of heat, Joule was able to use this experiment as a means of calculating the mechanical equivalent of heat. The numbers obtained from three series of experiments gave a mean value of 438 (in English measures 798); a value which agrees closely with the value 444 found by the compression of air, and does not differ from the value 424, found by the friction of water, more widely than can be explained by the causes of error inherent in these experiments.

§ 5. *Method of Experiment used by Thomson and Joule.*

The above-mentioned experiments of Joule, in which air contained in a receiver was expanded either by escaping into another receiver or into the atmosphere, shewed that the conclusions drawn under the assumption that air is a perfect gas are in close accordance with experience. If however we wished to know to what degree of approximation air or any other gas obeys the laws of perfect gases, and what are the laws of any variations that may occur from the conditions of a perfect gas, then the above mode of experiment is not sufficiently accurate; since the mass of the gas is too small compared with that of the vessels and other bodies which take part in the variation of heat, and therefore the sources of error derived from these have too great an influence on the result. A very ingenious method of making more accurate experiments was devised by W. Thomson, and the experiments were carried out by him and Joule with great care and skill.

Let us imagine a pipe, through which is forced a continuous current of gas. At one place in this let a porous plug be inserted, which so impedes the passage of the gas, that even when there is a considerable difference between the pressure before and behind the plug, it is only a moderate amount of gas, suitable for the experiment, which can pass through in a unit of time. Thomson and Joule used as plug a quantity of cotton wool or waste silk, which, as shewn in Fig. 21, was compressed between two pierced plates, *AB* and *CD*.

Let us now take two sections, *EF* and *GH*, one before and one behind the plug, but at such a distance that the unequal motions which may occur in the neighbourhood of the plug

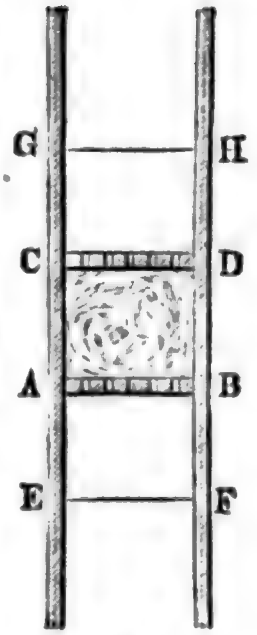

Fig. 21.

are not discernible, and there is only a uniform current of gas to deal with. Then the whole process of expansion, corresponding to the difference of pressure before and behind the plug, takes place in the small space between these two sections. If then the current of gas is kept uniform for a considerable time, a state of steady motion is produced, in which all the fixed parts of the apparatus keep their temperature unaltered, and neither take in nor give off heat. Then if, as was done by Thomson and Joule, we surround this space with a non-conducting substance, so that no heat can either pass into it from without or *vice versa,* the gas can only give out or take in the quantity of heat expended or generated in the process; and thus, even where this quantity is very small, a difference of temperature may exist sufficient to be easily noticed and accurately measured.

§ 6. *Development of the Equations relating to the above method.*

In order to determine theoretically the difference of temperature in the above case, we will first form the general equations determining the quantity of heat which the gas must have taken in, if the temperature at the second section is to have any required value. From this we can readily find the temperature at which the heat imparted will be nothing.

The separate parts of the process in the present case are connected partly with consumption, partly with generation of heat. Heat will be consumed in overcoming the frictional resistance due to the passage through the porous plug; whilst by the friction itself the same amount of heat will be generated. At certain points in the passage heat is consumed in increasing the velocity; whilst at other points heat is generated as the velocity decreases. To determine the quantity of heat which on the whole must be imparted to the gas, we may leave out of account the parts of the process which balance each other; since it is sufficient for our purpose to know what is the work which remains over as external work done or consumed, and at the same time the actual permanent change in the *vis viva* of the current. For this we need only consider the work done at the entrance of the gas into the space between the sections, i.e. at section EF, and also at the exit from that space, i.e. at section GH; and similarly the velocities of the current at those two sections.

With regard to the velocities, the difference between their *vis viva* can readily be calculated. If however they are at each section so small as they were in Thomson and Joule's experiments, their *vis viva* may be altogether neglected. It then remains only to determine the work done at the two sections. The absolute values of these quantities of work may be obtained as follows. Let us denote the pressure at section EF by p_1, and suppose the density of the gas at this section to be such that a unit-weight at this density has the volume v_1. Then the work done during the passage through the section of a unit-weight of the gas equals p_1v_1. Similarly the work done at section GH will be p_2v_2, where p_2 is the pressure and v_2 the specific volume at that section. These two quantities must however be affected with opposite signs. At section GH, where the gas is escaping from the given space, the external pressure has to be overcome, in which case the work done must be taken as positive; while in section EF, where the gas is entering the space and thus moving in the same direction as the external pressure, the work must be considered as negative. Thus the net external work performed on the whole will be represented by the difference $(p_2v_2 - p_1v_1)$.

We have now further to determine the quantity of heat, which a unit-weight of the gas must take in while it passes through the distance between the two sections; supposing the gas to have at the first section, where the pressure is p_1, the temperature T_1, and at the second section, where the pressure is p_2, the temperature T_2. For this purpose we must use the equation which applies to the case in which a unit-weight of the gas passes from a condition determined by the magnitudes p_1 and T_1 into that determined by the magnitudes p_2 and T_2, and performs in so doing the work $p_2v_2 - p_1v_1$. We therefore recur to equation (2), in which the symbol w, denoting the external work, must be replaced by $p_2v_2 - p_1v_1$; hence we have

$$Q = U_2 - U_1 + p_2v_2 - p_1v_1 \text{ ....} (10).$$

Here we need only to determine $U_2 - U_1$, for which purpose we can again use one of the differential equations for U set forth in the last chapter. In this case it is convenient to choose the differential equation in which T and p are the independent variables, i.e. equation (30) of Chapter IX.:

$$dU = \left(C_p - p\frac{dv}{dT}\right)dT - \left(T\frac{dv}{dT} + p\frac{dv}{dp}\right)dp.$$

In this equation we may put

$$p\frac{dv}{dT}dT + p\frac{dv}{dp}dp = pdv = d(pv) - vdp.$$

It thus takes the following form:

$$dU = C_p\,dT - \left(T\frac{dv}{dT} - v\right)dp - d(pv) \ldots\ldots.(11).$$

This equation must be integrated from the initial values T_1, p_1, to the final values T_2, p_2. The integration of the last term can be performed at once, and we may write:

$$U_2 - U_1 = \int\left[C_p\,dT - \left(T\frac{dv}{dT} - v\right)dp\right] - p_2v_2 + p_1v_1 \ldots.(12).$$

Substituting this value of $U_2 - U_1$ in equation (10), we obtain

$$Q = \int\left[C_p\,dT - \left(T\frac{dv}{dT} - v\right)dp\right] \ldots\ldots\ldots(13).$$

Here the expression under the integral sign is the differential of a function of T and p, since C_p satisfies equation (6) of Chapter VIII.:

$$\frac{dC_p}{dp} = -T\frac{d^2v}{dT^2}.$$

And thus the quantity of heat Q is completely determined by the initial and final values of T and p.

If we now introduce the condition corresponding to Thomson and Joule's experiments, viz. that $Q = 0$, then the difference between the initial and final temperatures is no longer independent of the difference between the initial and final pressures, but on the contrary the one can be found from the other. If we suppose both these differences indefinitely small, we may use instead of (13) the following differential equation:

$$dQ = C_p\,dT - \left(T\frac{dv}{dT} - v\right)dp.$$

If we here put $dQ=0$, we obtain the equation which expresses the relation between dT and dp, and which may be thus written:

$$\frac{dT}{dp} = \frac{1}{C_p}\left(T\frac{dv}{dT} - v\right) \quad\ldots\ldots\ldots\ldots\ldots\ldots(14).$$

If the gas were a perfect gas, and therefore $pv=RT$, we should have

$$\frac{dv}{dT} = \frac{R}{p} = \frac{v}{T},$$

hence the above equation would become

$$\frac{dT}{dp} = 0.$$

Thus in this case an indefinitely small difference of pressure produces no difference of temperature; and the same must of course hold if the difference of pressure is finite. Hence one and the same temperature must exist before and behind the porous plug. If on the contrary some difference of temperature is observed, it follows that the gas does not satisfy the law of Mariotte and Gay-Lussac, and by observing the values of these differences of temperature under various circumstances, definite conclusions may be formed as to the mode in which the gas departs from that law.

§ 7. *Results of the Experiments, and Equations of Elasticity for the gases, as deduced therefrom.*

The experiments made by Thomson and Joule in 1854* shewed that the temperatures before and behind the plug were never exactly equal, but exhibited a small difference, which was proportional to the difference of pressure in each case. With air at an initial temperature of about 15°, losses of temperature were observed, which, if the pressure were measured in atmospheres, could be expressed by the equation

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* *Phil. Trans.*, 1854, p. 321.

$$T_1 - T_2 = 0{\cdot}26^\circ\,(p_1 - p_2).$$

With carbonic acid the losses of heat were somewhat greater; with an initial temperature of about 19° they satisfied the equation

$$T_1 - T_2 = 1{\cdot}15^\circ\,(p_1 - p_2).$$

The differential equations corresponding to these two equations are as follows:

$$\frac{dT}{dp} = 0{\cdot}26 \text{ and } \frac{dT}{dp} = 1{\cdot}15 \;\ldots\ldots\ldots\ldots(15.)$$

In a later series of experiments, published in 1862*, Thomson and Joule took special pains to ascertain how the cooling effect varies when different initial temperatures are chosen. For this purpose they caused the gas, before reaching the porous plug, to pass through a long pipe surrounded by water, the temperature of which could be kept at will to anything up to boiling point. The result showed that the cooling was less at high than at low temperatures, and in the inverse ratio of the squares of the absolute temperatures. For atmospheric air and carbonic acid they arrived at the following complete formulae, in which a is the absolute temperature of freezing point, and the unit of pressure is the weight of a column of quicksilver 100 English inches high:

$$\frac{dT}{dp} = 0{\cdot}92\left(\frac{a}{T}\right)^2 \text{ and } \frac{dT}{dp} = 4{\cdot}64\left(\frac{a}{T}\right)^2.$$

If one atmosphere is taken as unit of pressure, these formulae become

$$\frac{dT}{dp} = 0{\cdot}28\left(\frac{a}{T}\right)^2 \text{ and } \frac{dT}{dp} = 1{\cdot}39\left(\frac{a}{T}\right)^2 \ldots\ldots\ldots(16).$$

With hydrogen Thomson and Joule observed in their later researches that a slight heating effect took place instead of cooling. They have however deduced no exact formula for this gas, because the observations were not sufficiently accurate.

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* *Phil. Trans.*, 1862, p. 579.

If in the two formulae for $\frac{dT}{dp}$, given in (16), we substitute for the numerical factor a general symbol A, they combine into one general formula, viz.

$$\frac{dT}{dp} = A\left(\frac{a}{T}\right)^2 \quad \text{.....................} (17).$$

Substituting in equation (14), we obtain

$$T\frac{dv}{dT} - v = AC_p\left(\frac{a}{T}\right)^2 \quad \text{..................} (18).$$

According to Thomson and Joule, this equation should be employed for gases as actually existing, in place of the equation referring to perfect gases,

$$T\frac{dv}{dT} - v = 0,$$

if we wish to express the relation which exists between the change of volume and temperature when the pressure is kept constant.

If C_p is taken as constant, equation (18) can be integrated immediately. Now it is only for perfect gases that it has really been proved that the specific heat C_p is independent of the pressure; and similarly it is only for perfect gases that the conclusion derived from Regnault's experiments is strictly true, viz. that C_p is also independent of the temperature. If however a gas differs very slightly from the condition of a perfect gas, C_p will have values differing very slightly from a constant, and these differences may be taken as quantities of the same order. Since in addition the whole term containing C_p is only another small quantity of the same order, the differences produced in the equation by the differences of C_p will be small quantities of a higher order, and such may in what follows be neglected; thus we may take C_p as constant. Then multiplying the equation by $\frac{dT}{T^2}$, and integrating, we have

$$\frac{v}{T} = -\tfrac{1}{3}AC_p\frac{a^2}{T^3} + P,$$

or
$$v = PT - \tfrac{1}{3} AC_p \left(\frac{a}{T}\right)^2 \text{ ....(19)},$$

where P is the constant of integration, which in the present case may be considered as a function of the pressure p.

According to the law of Mariotte and Gay-Lussac we should have
$$v = \frac{R}{p} T \text{.......................(20)};$$

and it is therefore advantageous to give the function P the form
$$P = \frac{R}{p} + \pi,$$

where π represents another function of p which however can only be very small. Equation (19) then becomes
$$v = R\frac{T}{p} + \pi T - \tfrac{1}{3} AC_p \left(\frac{d}{T}\right)^2 \text{ ....(21)}.$$

This equation Thomson and Joule further simplified as follows. The mode in which the pressure and volume of a gas depend on each other varies less from the law of Mariotte according as the temperature is higher. Those terms of the foregoing equation which express this variation must thus become smaller as the temperature rises. The last term is the only one which actually fulfils this condition; the last but one, πT, does not fulfil it. Accordingly this term should not appear in the equation, and putting $\pi = 0$, we obtain
$$v = R\frac{T}{p} - \tfrac{1}{3} AC_p \left(\frac{a}{T}\right)^2 \text{ ....(22)}.$$

This is the equation which according to Thomson and Joule must be used for gases actually existing, in place of equation (20) which holds for perfect gases.

An exactly similar equation was previously deduced by Rankine*, in order to represent the variations from the law of Mariotte and Gay-Lussac, found by Regnault in the case of carbonic acid. This equation in its simplest form may be written

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* *Phil. Trans.*, 1854, p. 336.

$$pv = RT - \frac{a}{Tv} \quad\text{..................}(23),$$

in which a like R is constant.

If we divide this equation by p, and in the last term, which is very small, replace the product pv by the very nearly equal product RT, and finally write β for the constant $\frac{a}{R}$, we obtain

$$v = R\frac{T}{p} - \frac{\beta}{T^2},$$

which is an equation of the same form as (22).

§ 8. *On the Behaviour of Vapour during Expansion under Various Circumstances.*

As a further example of the different results which may be produced by expansion, we will consider the behaviour of saturated vapour. We will assume two conditions: (1) that the vapour expanding has to overcome a resistance equal to its whole force of expansion; (2) that it escapes into the atmosphere, and thus has only to overcome the atmospheric pressure. Under the last condition we may make a distinction according as the vapour is separate from liquid in the vessel from which it escapes, or is in contact with liquid, which continually replaces by fresh evaporation the vapour which is lost. In all three cases we will determine the quantity of heat, which must be given to or taken from the vapour during expansion, in order that it may continue throughout at maximum density.

First then let us suppose a vessel to contain a unit-weight of saturated vapour, and let this vapour expand, *e.g.* by pushing a piston before it. In so doing let it exert upon the piston the whole expansive force which it possesses at each stage of its expansion. For this it is requisite only that the piston should move so slowly that the vapour which follows should always be able to equalize its expansive force to that of the vapour which remains behind in the vessel. The quantity of heat Q, which must be imparted to this vapour, if it expands so far as that its temperature falls from a given initial value T_1 to a value T_2, is simply found by the equation

$$Q = \int_{T_1}^{T_2} h\,dT \quad\text{..................}(24).$$

Here h is the magnitude introduced in Chapter VI., and named the Specific Heat of Saturated Vapour. If, as is the case with most vapours, h has a negative value, the foregoing integral, in which the upper limit is less than the lower, represents a positive quantity.

In the case of water, h is given by formula (31) of Chapter VI., viz.,

$$h = 1{\cdot}013 - \frac{800{\cdot}3}{T}.$$

Applying this formula it is easy to calculate the value of Q for any two temperatures T_1 and T_2. For example let us assume that the steam has an initial pressure of 5 or of 10 atmospheres, and that it expands until its pressure has fallen to one atmosphere; then by Regnault's tables we must put $T_1 = a + 152{\cdot}2$, or $= a + 180{\cdot}3$ respectively, and $T_2 = a + 100$; we thus obtain the values $Q = 52{\cdot}1$ or $= 74{\cdot}9$ units of heat respectively.

In the second case we suppose that a vessel contains a unit-weight of saturated vapour apart from liquid, and at a temperature T_1 which is above the boiling point of the liquid; and that an opening is made in the vessel, so that the vapour escapes into the atmosphere. Let us proceed to a distance beyond the opening such that the pressure of the vapour is there only equal to the atmospheric pressure. To insure that the current of vapour shall expand in the proper manner, let the vessel be fitted at the opening with a trumpet-shaped mouth $KPQM$ (Fig. 22.) This mouth is not actually needed in order that the equations which follow may hold, but merely serves to facilitate the conception. Let KLM be a surface within this mouth, such that the pressure of the vapour is there only equal to atmospheric pressure, and its velocity so small that its *vis viva* may be neglected. We will further assume that the heat generated by the friction of the vapour against the edge of the opening and the surface of the mouth is not dissipated, but again imparted to the vapour.

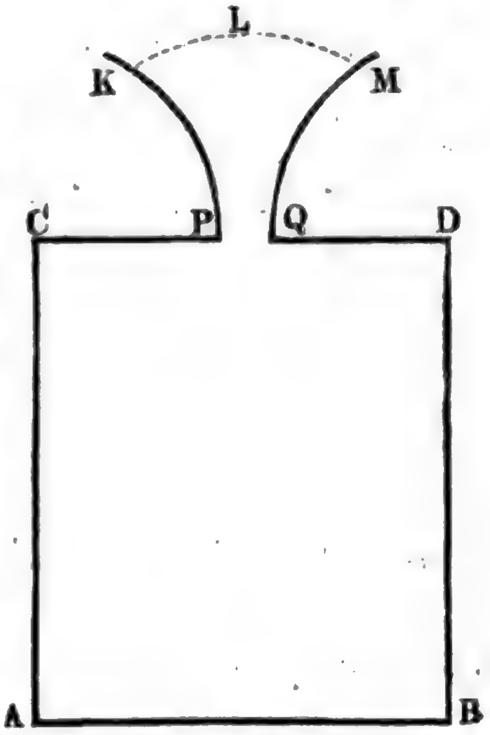

Fig. 22.

Now to determine the quantity

of heat which must be imparted to the vapour during expansion, if it is to remain throughout in the saturated condition, we will again apply the general equation (2); which gives, if in this case we denote the heat by Q',

$$Q' = U_2 - U_1 + W \quad \ldots\ldots\ldots\ldots\ldots\ldots (25);$$

here U_1 is the energy of the vapour in its initial condition within the vessel, U_2 the energy of the vapour in its final condition at the surface KLM, and W the external work done in overcoming the pressure of the atmosphere.

The energy of a unit-weight of saturated vapour at temperature T is given by the value of U in equation (37) of Chapter IX., if we there put $m = M = 1$. It is

$$U = U_0 + \int_{T_0}^{T} \left(C - p\frac{d\sigma}{dT}\right) dT + \rho\left(1 - \frac{p}{T\frac{dp}{dT}}\right).$$

First give to T the initial value T_1, and let p_1, $\left(\frac{dp}{dT}\right)_1$, and ρ_1 be the values of p, $\frac{dp}{dT}$, and ρ corresponding to this temperature. Again let T have the final value T_2, and let p_2, $\left(\frac{dp}{dT}\right)_2$, and ρ_2 be the corresponding values. Then subtracting these two equations from each other we have

$$U_2 - U_1 = \int_{T_1}^{T_2} \left(C - p\frac{d\sigma}{dT}\right) dT + \rho_2\left[1 - \frac{p_2}{T_2\left(\frac{dp}{dT}\right)_2}\right] - \rho_1\left[1 - \frac{p_1}{T_1\left(\frac{dp}{dT}\right)_1}\right] \quad \ldots\ldots\ldots (26).$$

The external work which results from the overcoming of the atmospheric pressure p_2, during an expansion from volume s_1 to volume s_2, is given by the equation

$$W = p_2(s_2 - s_1).$$

We will give another form to this expression. If, as in Chapter VI., we put $s = u + \sigma$, where σ is the specific volume of the liquid, the equation becomes

$$W = p_2 (u_2 - u_1) + p_2 (\sigma_2 - \sigma_1).$$

Substituting for u the expression given in equation (13), Chapter VI., we have

$$W = p_2 \left[\frac{\rho_2}{T_2 \left(\frac{dp}{dT}\right)_2} - \frac{\rho_1}{T_1 \left(\frac{dp}{dT}\right)_1} \right] + p_2 (\sigma_2 - \sigma_1) \ldots\ldots (27).$$

Now substituting in (25) the value of $U_2 - U_1$ from (26), and of W from (27), we arrive at the equation

$$Q' = \int_{T_1}^{T_2} \left(C - p \frac{d\sigma}{dT} \right) dT + \rho_2 - \rho_1 + \frac{\rho_1}{T_1 \left(\frac{dp}{dT}\right)_1} (p_1 - p_2)$$
$$+ p_2 (\sigma_2 - \sigma_1) \ldots\ldots\ldots (28).$$

Here the heat is expressed in mechanical units. To express it in ordinary heat units the right-hand side must be divided by E. As before we will put $\frac{C}{E} = c$; $\frac{\rho}{E} = r$. At the same time, since σ is a small quantity and varies very slightly, we will neglect the quantities $\frac{d\sigma}{dT}$ and $(\sigma_2 - \sigma_1)$. Thus we obtain

$$Q' = \int_{T_1}^{T_2} c dT + r_2 - r_1 + \frac{r_1}{T_1 \left(\frac{dp}{dT}\right)_1} (p_1 - p_2) \ldots\ldots\ldots (29).$$

This equation is well adapted for the numerical calculation of Q, since the quantities which it contains have all been determined experimentally for a considerable number of liquids.

For water we have according to Regnault

$$c + \frac{dr}{dT} = 0{\cdot}305;$$

whence

$$\int_{T_1}^{T_2} c dT + r_2 - r_1 = -0{\cdot}305 (T_1 - T_2).$$

The quantities in the last term of equation (29) are also sufficiently known, so that the whole calculation is easy. For example if we take the initial temperature at five or ten atmospheres, we have $Q' = 19{\cdot}5$ or $= 17{\cdot}0$ units of heat respectively.

Since Q' is positive, it follows that in this case also heat must be imparted to the vapour, not taken from it, if no part of it is to be allowed to condense; which condensation might take place not only at the opening, but equally well inside the vessel. The quantity of vapour so condensed would however be less than in the first case, because Q' is less than Q.

It may easily happen that the above equations give a larger quantity of heat for an initial pressure of five than of ten atmospheres. The reason is that at five atmospheres the volume of the vapour is already very small; and the diminution of volume, when the pressure is raised to ten atmospheres, is so small that the corresponding increase of work during the escape of the vapour is more than balanced by the excess of the free heat in the vapour at 180·3° over that in the vapour at 152·2°.

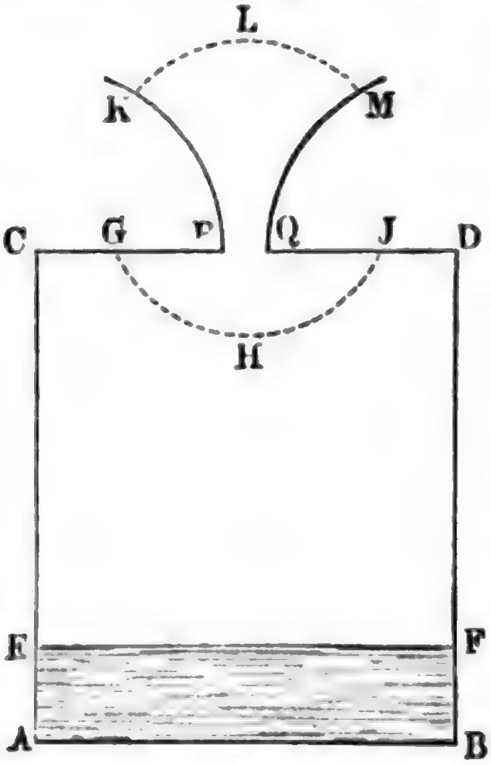

Fig. 23.

Lastly let us take the third case, in which the vessel contains liquid as well as vapour. Let the vessel *ABCD* (Fig. 23) be filled to the level *EF* with liquid, and above this with vapour. Let *PQ* be the opening of escape, fitted, as in the last case, with the trumpet-shaped mouth *KPQM*, to regulate the spreading out of the current of vapour. Let there be some source of heat which keeps the liquid at a constant temperature T_1, so that it continually gives off new vapour to replace that which escapes, and thus the conditions of the escape remain always the same.

This last circumstance makes an important distinction between this case and the foregoing. The pressure, which the vapour newly given off exerts on that already existing, performs work during the escape of the vapour, which must be brought into the calculation as negative external work.

Let *GHJ* be a surface at which the vapour which passes through has still the same expansive force p_1, temperature T_1, and specific volume s_1 which exist within the vessel, and at which the new vapour is given off. Again let *KLM* be a surface at which the vapour passing through has simply the expansive force equal to the atmospheric pressure p_2. At both surfaces we shall assume the velocity to be so small that its *vis viva* may be neglected. In its passage from one surface to the other, the vapour must continually have just that measure of heat given to it or taken from it, which is necessary in order to keep it wholly in the gaseous condition, and completely saturated, and also in order that at the surface *KLM* it may have the temperature T_2 corresponding to the pressure p_2 (*i.e.* the boiling temperature of the liquid), and the specific volume s_2 belonging to that temperature. We have now to enquire how large this quantity of heat Q'' must be for each unit-weight of the escaping vapour.

To determine this we may proceed as in the last case, remembering that we have now a different value for the external work. This value is the difference between the work done at the surface *GHJ*, through which passes a volume of vapour s_1 at pressure p_1, and that done at the surface *KLM*, through which passes a volume s_2 at pressure p_2. It is thus given by the equation

$$W = p_2 s_2 - p_1 s_1.$$

Putting once more

$$s = u + \sigma = \frac{\rho}{T\dfrac{dp}{dT}} + \sigma,$$

we have

$$W = \frac{p_2 \rho_2}{T_2 \left(\dfrac{dp}{dT}\right)_2} - \frac{p_1 \rho_1}{T_1 \left(\dfrac{dp}{dT}\right)_1} + p_2 \sigma_2 - p_1 \sigma_1 \ldots\ldots (30).$$

If we now form for Q'' an equation of the same form as (25), and in it substitute for $U_2 - U_1$ the expression given in (26), and for W the expression given above, the main terms in these two expressions cancel each other, and there remains

$$Q''=\int_{T_1}^{T_2}\left(C-p\frac{d\sigma}{dT}\right)dT+\rho_2-\rho_1+p_2\sigma_2-p_1\sigma_1 \dots (31).$$

If we transform this equation so that it refers not to mechanical but to ordinary units of heat, and neglect the terms containing σ, we arrive at the simple equation

$$Q''=\int_{T_1}^{T_2} c\,dT+r_2-r_1 \dots\dots\dots\dots (32).$$

For water the equation takes the form

$$Q''=-0{\cdot}305\,(T_1-T_2)\,;$$

and if we calculate the numerical values of Q'' for an initial pressure of five or of ten atmospheres, we obtain

$Q''=-15{\cdot}9$ or $=-24{\cdot}5$ units of heat respectively.

Since the values of Q are negative, it follows that in this case heat must be taken out of the vapour, not imparted to it. If this withdrawal of heat does not take place to a sufficient extent at any place under consideration, then the steam is there hotter than 100° and therefore superheated. Here it is of course assumed that nothing but steam passes through the first surface *GHJ*, and thus that there are no particles of liquid mechanically carried off by the steam, as may happen during violent ebullition.

CHAPTER XI.

APPLICATION OF THE MECHANICAL THEORY OF HEAT TO THE STEAM-ENGINE.

§ 1. *Necessity of a new Investigation into the Theory of the Steam-Engine.*

Since the altered views as to the nature and action of Heat, which are comprised under the name of the Mechanical Theory of Heat, had their first origin in the known fact that heat can be applied to produce mechanical work, it might have been at once expected that the theory so formed would conversely serve to place this application of heat in a clearer light. In particular the more general point of view thus obtained would make it possible to pass a more certain judgment upon the particular machines used for this application, as to whether they already completely fulfilled their purpose, or whether and how far they failed to do so.

To these reasons, which apply to all thermo-dynamic machines, are joined in the case of the most important of them, the steam-engine, certain special grounds, which make it desirable to undertake a new investigation into its working, derived from the mechanical theory of heat. This theory in fact, in the case of steam of maximum density, has brought to light certain important departures from the laws previously assumed as correct, or at least generally used for purposes of calculation.

On this head we need only refer to two results given in Chapter VI. In most of the recent writings on the steam-engine, amongst others the excellent work of de Pambour, the foundation of the theory has been taken to be the law of Watt, viz. that saturated steam when contained in a non-conducting vessel remains during all changes of volume steam of maximum density. In some later writings, after the publication of Regnault's researches on the heat required to evaporate water at different temperatures, the assumption is made that steam partly condenses during compression, and during expansion cools in a less degree than corresponds to the reduction of density, and therefore passes into the superheated condition. On the other hand it is proved in Chapter VI. that steam must behave in a way which is different from the first assumption and the exact opposite of the second assumption, viz. that it is superheated during compression, and is partly condensed during expansion.

Further it is assumed in the above writings, in default of more accurate means of determining the volume of a unit-weight of steam at different temperatures, that steam even at its maximum density still follows the law of Mariotte and Gay-Lussac. On the other hand it is shewn in Chapter VI. that it departs widely from that law.

These two points have naturally an important influence on the quantity of steam which passes from the boiler into the cylinder at each stroke, and on the behaviour of this steam during expansion. It is thus obvious that they are themselves sufficient to make it necessary that we should calculate in a different way from that hitherto adopted the amount of work which a given quantity of steam performs in the steam-engine.

§ 2. *On the Action of the Steam-Engine.*

In order to illustrate more clearly the series of processes which make up the action of a condensing steam-engine, and to bring out clearly the fact that they form a cyclical process, continually repeating itself in the same manner, the imaginary diagram (Fig. 24) may be employed. *A* is the boiler, the contents of which are kept uniformly at

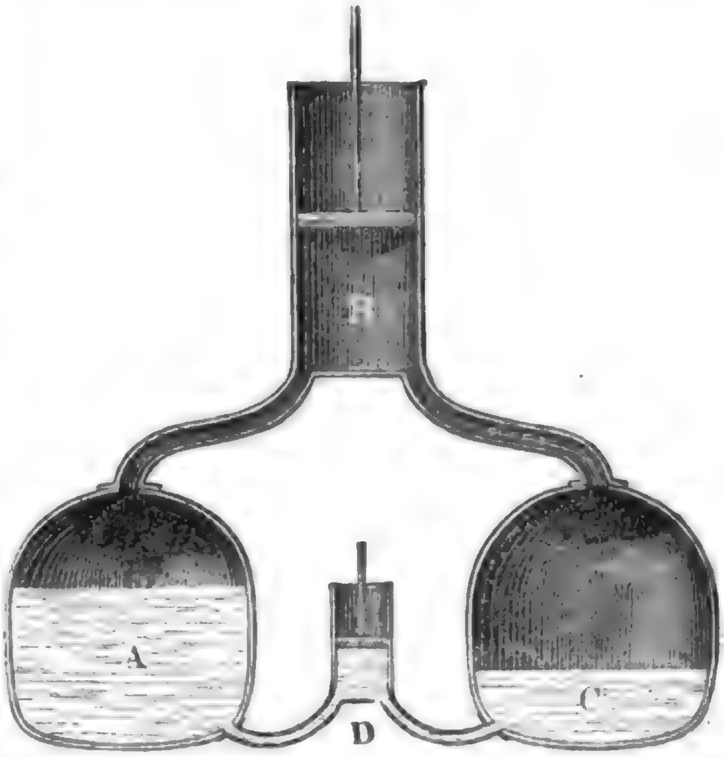

Fig. 24.

a constant temperature T, by means of a source of heat. From this boiler a part of the steam passes into the cylinder B, and drives the piston a certain distance upwards. Then the cylinder is shut off from the boiler, and the enclosed steam drives the piston still higher by expansion. The cylinder is now put in connection with the vessel C, which represents the condenser. It will be supposed that this condenser is kept cold, not by injected water, but by cooling from without: this makes no great difference in the results, but simplifies the treatment. The constant temperature of the condenser we may call T_0. During the connection of the cylinder with the condenser, the piston returns through the whole distance it has previously traversed; and thereby all the steam which has not of itself passed into the condenser is driven into it, and there condenses into water. It remains, in order to complete the cycle of operations, that this condensed water should be brought back again into the boiler. This is effected by the small pump D, the working of which is so regulated, that during the upward stroke of its piston it draws out of the condenser exactly as much water as has been brought into it by the condensation during the last stroke; and this water is then, by the downward stroke of its piston, forced back into the boiler. When it has here been heated once more to the temperature T_1, all is again restored to its initial condition, and the same series of processes may begin anew. Thus we have here to deal with a complete cyclical process.

In the common steam-engine the steam passes into the cylinder not at one end only, but at both ends alternately. The only difference thereby produced is, however, that during one up and down stroke of the piston two cyclical processes take place instead of one, and it is sufficient in this case to determine the work done during one process, in order to be able to deduce the whole work done during any given time. In the case of an engine without a condenser, we have only to assume that it is fed with water at 100°, and we may then suppose it replaced by an engine with a condenser, the temperature of the condenser being 100°.

§ 3. *Assumptions for the purpose of Simplification.*

For the purpose of this investigation we will assume, as has usually been done, that the cylinder is a non-conducting vessel, and so neglect the exchange of heat which takes place during each stroke between the walls of the cylinder and the steam.

The vapour within the cylinder can never be anything but steam of maximum density with a certain admixture of water. For it is evident from the conclusions of Chapter VI., that during the expansion which takes place in the cylinder after it is shut off from the boiler the steam cannot pass into the superheated condition, because no heat is imparted to it from without; but must rather partially condense. It is true that there are certain other processes, to be mentioned later, which tend to produce a slight super-heating; but this is prevented from taking place by the fact, that the steam always carries with it into the cylinder a certain amount of water in the form of spray, with which it remains in contact. The exact amount of this water is of no importance; and since for the most part it is diffused through the steam in fine drops, and therefore readily participates in the changes of temperature which the steam undergoes during expansion, no important error will be introduced if at each moment under consideration we assume that the temperature of the whole mass of vapour in the cylinder is the same.

Further, to avoid too great complexity in the formulæ, we will first determine the whole work done by the steam pressure, without examining how much of this is actually useful work, and how much is expended on the engine itself in overcoming friction, and in actuating the pumps required, besides the one shewn in the figure, for the proper working of the machine. This latter part of the work may be subsequently determined and deducted from the whole, in the manner shown later on. It may further be remarked with regard to the friction between the piston and cylinder, that the work expended upon this is not to be regarded as wholly lost. For since heat is generated by this friction, the inside of the cylinder is thereby kept hotter than it otherwise would be, and the power of the steam increased accordingly.

Lastly, since it is desirable to understand the working of the most perfect machine possible, before enquiring into the influence of the various imperfections which occur in practice, we will in this preliminary investigation make two further assumptions, which may afterwards be withdrawn. The first is that the inlet pipe from the boiler to the cylinder, and the outlet pipe to the condenser or to the atmosphere, are so large, or else the speed of the engine so slow, that the pressure within the end of the cylinder connected with the boiler is always equal to the pressure in the boiler itself; and similarly that the pressure within the other end is always equal to that in the condenser, or to the atmospheric pressure as the case may be. The second is that there are no clearance or waste spaces sufficient to affect the result.

§ 4. *Determination of the Work done during a single stroke.*

Under the conditions just enumerated the amount of work done during the cyclical process corresponding to a single stroke may be written down by help of the results obtained in Chapter VI. without further calculation, and their sum comprised in a simple expression.

Let M be the whole quantity of vapour which passes from the boiler to the cylinder during one stroke; of this let the part m_1 be in the form of steam and the remainder $M-m_1$ in the form of water. The space which this mass occupies will be (by Ch. VI., § 1) $m_1 u_1 + M\sigma$, where u_1 represents the value of u corresponding to T_1, while σ is taken as constant and therefore has no suffix. The piston has therefore been raised so far that this amount of space is left under it; and since this takes place at the pressure p_1 corresponding to T_1, the work done during the first process, which we may call W_1, is given by the following equation:

$$W_1 = m_1 u_1 p_1 + M\sigma p_1 \qquad \text{.................(1).}$$

Let the expansion which succeeds to this continue so far that the temperature of the vapour enclosed in the cylinder falls from the value T_1 to a value T_2. The work done during this expansion, which we may call W_2, is given directly by equation (62) of Chapter VI., if we there take T_2 for the final temperature, and corresponding values for the other quantities involved. Thus

$$W_2 = m_1(\rho_1 - u_1 p_1) - m_2(\rho_2 - u_2 p_2) + MC(T_1 - T_2) \ldots\ldots (2).$$

On the return stroke of the piston, which now begins, the vapour, which at the end of the expansion occupied the space $m_2 u_2 + M\sigma$, is driven out of the cylinder into the condenser, overcoming the constant resistance p_0. The negative work thus performed is therefore given by the equation

$$W_3 = -m_2 u_2 p_0 - M\sigma p_0 \ldots\ldots\ldots\ldots\ldots\ldots (3).$$

Now let the piston of the small pump rise until it leaves under it the space $M\sigma$; the pressure then continues to be the pressure p_0 of the condenser, and the work done is

$$W_4 = M\sigma p_0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4).$$

Finally, during the descent of this piston, the pressure p_1 of the boiler has to be overcome, and we have therefore the negative work

$$W_5 = -M\sigma p_1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5).$$

Adding these five equations we have for the whole work done during the cyclical process by the steam pressure, or in other words by the heat, which work we may call W', the following expression :

$$W' = m_1\rho_1 - m_2\rho_2 + MC(T_1 - T_2) + m_2 u_2 (p_2 - p_0) \ldots (6).$$

From this equation we must eliminate m_2. If for u_2 we substitute the value given by equation (13) Chapter VI., viz.

$$u_2 = \frac{\rho_2}{T_2\left(\frac{dp}{dT}\right)_2},$$

then m_2 only occurs in the product $m_2\rho_2$; for which equation

(55) Chapter VI. gives, if we substitute therein ρ and C for r and c, the expression

$$m_2\rho_2 = m_1\rho_1 \frac{T_2}{T_1} - MCT_2 \log \frac{T_2}{T_1}.$$

Substituting this expression we obtain an equation in which all the quantities on the right-hand side are known, since the masses M and m_1, and the temperatures T_1, T_2, and T_0 are supposed to be known directly, and the quantities ρ, p, and $\frac{dp}{dT}$ are assumed to be known as functions of temperature.

§ 5. *Special Forms of the Expression found in the last section.*

If in equation (6) we put $T_2 = T_1$, we obtain the work done in the case where the machine works without expansion, viz.

$$W' = m_1 u_1 (p_1 - p_0) \text{.....................} (7).$$

If on the other hand we assume that the expansion continues until the steam has cooled by expanding from the temperature of the boiler down to that of the condenser (an assumption which cannot be realized in practice, but forms the limiting case to which we may approach as near as is practicable) we have only to put $T_2 = T_0$; whence we have

$$W' = m_1\rho_1 - m_0\rho_0 + MC(T_1 - T_0) \text{...........} (8).$$

Eliminating $m_0\rho_0$ from this equation by means of the same equation (55) Chapter VI., in which we must also put $T_2 = T_0$, we have

$$W' = m_1\rho_1 \frac{T_1 - T_0}{T_1} + MC\left(T_1 - T_0 + T_0 \log \frac{T_0}{T_1}\right) \text{......} (9).$$

§ 6. *Imperfections in the Construction of the Steam-Engine.*

With all steam-engines as actually constructed the expansion falls much below the maximum value given at the end of the last section. If for example we take the temperature of the boiler at 150°, and that of the condenser at 50°, then if the temperature of the steam in the cylinder is to be lowered by expansion to the temperature of the condenser, the steam must be expanded (by the table given in § 13 of Chapter VI.) to twenty-six times its original volume. In practice, on account of the many evils attending too high an expansion, steam is not expanded beyond three or four times its volume in general, or ten times at the very utmost. Such an expansion, with an initial temperature of 151°, is shewn by the same tables to lower the temperature to 100°, or 75° at the utmost, instead of to 50°.

Besides this imperfection, which has already been taken account of in the above investigation and included in equation (6), the steam-engine is subject to several others, two of which have been already expressly excluded from consideration. These are, first the fact that the pressure in one end of the cylinder is less than that in the boiler, and in the other greater than that in the condenser, and secondly the presence of waste spaces. We must now extend our previous investigations so as to include these further imperfections.

The influence upon the work done of the difference between the boiler and cylinder pressures has been investigated most fully by Pambour in his work *Théorie des Machines à Vapeur*. The author may therefore be allowed, before himself entering on the subject, to reproduce the most important of these investigations, only making some changes in the notation and omitting the quantities which refer to friction. It will thus be easier to shew how far Pambour's results are no longer in accordance with our present knowledge on the subject of heat, and at the same time to connect with it the new method of investigation, which in the author's opinion must take its place.

§ 7. *Pambour's Formulae for the relation between Volume and Pressure.*

Pambour's theory has its foundation in the two laws already mentioned, which at that time were generally applied to the case of steam. The first is the law of Watt, viz. that the sum of free and latent heat is always constant. From this law, as already mentioned, was drawn the conclusion that if a certain quantity of steam at maximum density were inclosed in a non-conducting vessel, and the contents of this vessel then increased or diminished, the steam would neither be superheated nor partially condensed, but would remain precisely at maximum density; and that this would take place without any reference to the way in which the change of volume was produced, or to whether the steam had to overcome a resistance corresponding to its expansive force, or not. This was the condition of things which Pambour supposed to exist in the steam cylinder; and he also assumed that no change of importance would be occasioned by the presence of the particles of water which are always mixed with the steam.

Next, to determine more closely the connection between volume and temperature, or between volume and pressure, in the case of steam at maximum density, Pambour applied further the law of Mariotte and Gay-Lussac. If we take the volume of a kilogram of steam at 100° and at maximum density to be 1·696 c. m., as given by Gay-Lussac, and if we remember that the corresponding pressure of one atmosphere represents a weight of 10333 kilograms to the square metre; and if for any other temperature T we call v the volume and p the pressure; then the law of Mariotte and Gay-Lussac leads to the following equation:

$$v = 1{\cdot}696 \times \frac{10333}{p} \times \frac{273 + T}{273 + 100} \quad\ldots\ldots\ldots\ldots \quad (10).$$

Here we have only to substitute for p the value given by the table of pressures, and we can then determine the volume corresponding to any temperature, provided the foregoing assumptions are correct.

Since in the formulae for the work done by the steam-engine $\int p\,dv$ plays a principal part, it was necessary for the convenient treatment of this integral, that the simplest possible relation between p and v should be used. The equations which would have been obtained, if it had been sought to eliminate the temperature T from the foregoing equation by means of one of the ordinary empirical formulae for p, would have been too complicated: Pambour accordingly preferred to form a special empirical formula for the purpose, and following the example of Navier he gave it the following general form:

$$v = \frac{B}{b + p} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11),$$

where B and b are constants. These constants he endeavoured to fix so that the volumes calculated by this formula might agree as nearly as possible with those calculated by the formula given above. As however sufficient accuracy cannot thus be arrived at in the case of all the pressures which are met with in the steam-engine, he made use of two different formulae in the cases of engines with and without condensers. The first, for condensing engines, is as follows:

$$v = \frac{20000}{1200 + p} \text{ .... } (11a),$$

This agrees best with the formula (10) for pressures between $\frac{2}{3}$ and $3\frac{1}{2}$ atmospheres, but may be applied within somewhat wider limits, say $\frac{1}{2}$ and 5 atmospheres. The second, for non-condensing engines, is as follows:

$$v = \frac{21232}{3020 + p} \text{ .... } (11b).$$

This is most accurate between 2 and 5 atmospheres, and may be applied anywhere between $1\frac{1}{2}$ and 10 atmospheres.

§ 8. *Pambour's Determination of the Work done during a single stroke.*

The quantities needed for determining the work done, and depending on the dimensions of the engine, will be here denoted in a manner somewhat differing from that of Pambour. The whole space within the cylinder, including the waste space, which is left open for steam during a single stroke, we shall call v'. The waste space we shall call $\epsilon v'$ and the space swept through by the piston $(1 - \epsilon) v'$. That part of the whole space, which is left open for the steam up to the moment when the cylinder is shut off from the boiler, again inclusive of the waste space, we shall call ev'. Then the space swept through by the piston during the entrance of steam will be denoted by $(e - \epsilon) v'$, and that swept through during expansion by $(1 - e) v'$.

First to determine the work done during the entrance of the steam. For this purpose we must know the actual pressure in the cylinder at this time, which must be less than that in the boiler, otherwise there would be no flow from one into the other. The amount of this difference cannot however be fixed in general terms, because it depends not only on the construction of the engine, but also on how widely the valve in the steam pipe has been opened by the engineer, and on the speed with which the engine is moving. By a change in these circumstances the difference may be made to vary within wide limits. Again the pressure in the cylinder may not remain constant during the whole time the steam is entering, because the speed of the piston, and also the opening left by the valve, may be made to vary during this time.

With reference to this latter point Pambour assumes that the mean pressure, to be used for determining the work done, may with sufficient accuracy be taken to be the same as the final pressure which exists in the cylinder at the moment when it is shut off from the boiler. The author does not think it desirable to introduce into the general formulae an assumption of this kind, although in the absence of more exact data it may fairly be resorted to for the purpose of actual calculations; but he is bound to follow Pambour's method, in order to complete the exposition of his theory.

The actual pressure at the moment when the steam is shut off, Pambour determines by means of his equation, as given above, between volume and pressure; assuming that special observations have been made to determine the quantity of steam which passes from the boiler to the cylinder during an unit of time, and therefore during each stroke. We will, as before, denote by M the whole quantity which passes into the cylinder during one stroke, and by m the portion which is in the condition of steam. As this quantity M, of which Pambour only recognizes the part which is in the condition of steam, fills at the moment when the cylinder is closed the space ev', we have by equation (11),

$$ev' = \frac{mB}{b + p_2} \text{ ....} (12),$$

where p_2 is the pressure in the cylinder at that moment. Hence

$$p_2 = \frac{mB}{ev'} - b \text{ ....} (12a).$$

If we multiply this equation by $(e - \epsilon)\,v'$, which is the space swept through by the piston up to this moment, we have the following equation for the first part of the work done:

$$W_1 = mB \times \frac{e - \epsilon}{e} - v' (e - \epsilon) b \text{ ....(13).}$$

The law of variation of the pressure during the expansion is also given by equation (11). If v is the volume and p the pressure at any moment, then

$$p = \frac{mB}{v} - b.$$

This expression we must substitute in $\int pdv$, and then integrate this from $v = ev'$ to $v = v'$. Thence we obtain for the second part of the work done

$$W_2 = mB \log \frac{1}{e} - v' (1 - e) b \text{ ....(14).}$$

Next, to determine the negative work done by the resistance during the return stroke, we must know the value of that resistance. Without entering at present into the question how this resistance is related to the pressure in the condenser, we will denote the mean pressure by p_0; then the work done will be given by

$$W_3 = - v' (1 - \epsilon) p_0 \text{ ....(15).}$$

Finally there remains the work which must be expended in forcing back into the boiler the quantity of liquid M. Pambour has taken no special account of this work, but included it with the friction of the engine. Since, however, for the sake of completing the cycle of operations, it has been included in the author's formulae, it will be investigated here in order to facilitate the comparison. If p_1 be the pressure in the boiler, and p_0 in the condenser, then equations (4) and (5) show, as in the example already considered, that this work is on the whole given by

$$W_4 = - M\sigma (p_1 - p_0) \text{ ....(16).}$$

For the present case, where p_0 is not the pressure in the condenser itself, but in the end of the cylinder which is open to the condenser, this equation is not quite exact; but since on account of the smallness of σ the value of the whole expression is almost too small to be taken into account, *à fortiori* we may neglect an error which is small even in comparison with that value; and we shall therefore retain the expression in the form given above.

Adding these four several quantities of work together, we obtain the following expression for the whole work done during the cyclical process:

$$W = mB\left(\frac{e-\epsilon}{e} + \log\frac{1}{e}\right) - v'(1-\epsilon)(b+p_0) - M\sigma(p_1 - p_0) \quad \text{.........(17)}.$$

§ 9. *Pambour's Value for the Work done per Unit-weight of Steam.*

If instead of the work done in one stroke, during which the quantity of steam used is m, we prefer to find the work done per unit-weight of steam, all that is needed is to divide the foregoing value by m. Let us denote by l the fraction $\frac{M}{m}$, which gives the ratio of the whole mass which passes into the cylinder to that part of it which is in the form of steam, and is therefore somewhat greater than 1; by V the fraction $\frac{v'}{m}$, i.e. the space which on the whole is occupied by the unit-weight of steam in the cylinder; and by W the fraction $\frac{W'}{m}$, i.e. the work done per unit-weight of steam. Then we have

$$W = B\left(\frac{e-\epsilon}{e} + \log\frac{1}{e}\right) - V(1-\epsilon)(b+p_0) - l\sigma(p_1 - p_0) \quad \text{.........(18)}.$$

In this equation there is only one term which involves the volume V, and this contains V as a factor. Since this term is negative, it follows that the work, which can be obtained from one unit-weight of steam, is the greatest, other things being equal, when the volume which that steam occupies in the cylinder is the least possible. The least value of this volume, to which we may continually approximate, but can never exactly obtain, is that which is given by the assumption that either the engine goes so slowly, or the steam-pipe is so large, that the pressure in the cylinder is as great as that in the boiler. This then gives the maximum quantity of work. If with an equal admission of steam the speed of the engine is greater, or if with equal speed the admission of steam is less, then in each case a less quantity of work is obtained from the same quantity of steam.

§ 10. *Changes in the Steam during its passage from the Boiler into the Cylinder.*

Before we pass on to treat the same connected series of processes on the principles of the Mechanical Theory of Heat, it will be advantageous to consider one of them, which requires a special investigation of its own, in order to fix beforehand the results which refer to it. This process is the flow of the steam into the clearance or waste space and into the cylinder, in the case when it has a smaller pressure to overcome than that which forces it out of the boiler.

The steam as it comes from the boiler passes first into the waste space; there it compresses the steam of less density which remains over from the last stroke, fills up the space thus obtained, and then acts upon the piston; this, according to the assumption, on account of its comparatively lighter load recedes so fast, that the steam cannot follow it quickly enough to keep the density in the cylinder the same as in the boiler. Under such circumstances, if nothing but saturated steam escaped from the boiler, this would become superheated in the cylinder, inasmuch as the *vis viva* of the flow would be transformed into heat; but since the steam always carries with it small particles of water, the superabundant heat goes to vaporize a part of these, and the steam thus remains in the saturated condition.

We must now consider the following problem: Given the initial condition of the whole mass under consideration, as well that already found in the waste space as that which is newly received from the boiler; given also the amount of work which is done during the entrance of the steam by the pressure which acts on the piston; lastly given the pressure which exists at the moment when the boiler is shut off from the cylinder; then to determine what proportion of the mass within the cylinder is at that moment in the condition of steam.

Let μ be the mass which exists in the waste space before the entrance of the steam; for the sake of generality we will assume this to be partly in the liquid, partly in the gaseous condition, and will call the latter part μ_0. The pressure of this steam may for the moment be denoted by p_0, and the corresponding absolute temperature by T_0, without implying thereby that these are exactly the same values as hold for the same quantities within the condenser. Let p_1 and T_1 be, as before, the pressure and temperature in the boiler, M the mass which flows from the boiler into the cylinder, and m_1 the part of M which is in the condition of steam. The pressure exerted on the piston during the entrance of the steam need not, as already explained, be constant. We will call p_0 the mean pressure, by which the space swept through by the piston during the entrance of the steam must be multiplied, in order to obtain the same amount of work as is actually done by the varying pressure. Let p_2 be the actual pressure in the cylinder at the moment when the steam is cut off, T_2 the corresponding temperature. Lastly let m_2 be the magnitude we have to determine, viz. the part of the whole mass $M + \mu$ within the cylinder, which is in the condition of steam.

To determine this quantity, let us suppose the mass $M+\mu$ to be brought back to its initial condition in any way whatever, e.g. the following. Let the gaseous part m_2 be condensed in the cylinder by the fall of the piston, it being assumed that the piston can force itself even into the waste space; at the same time let the mass have such a quantity of heat continuously imparted to it, that its temperature T_2 remains constant. Then let the part M of the whole liquid mass be forced back into the boiler, where it again takes up its original temperature T_1. We have now within the boiler the same condition of things as before the flow of the steam, since every part of the boiler has its original temperature; and therefore the proportions of liquid and steam must be the same as at the commencement. Whether the individual molecules, which are in the gaseous and in the liquid condition, are exactly the same as at the commencement does not concern us; we make no distinction between these, and never enquire what molecules, but simply how many molecules, are in each of the two conditions.*

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* If it be wished that exactly the same molecules should be in the

Let the mass μ, which is not forced back into the boiler, be first cooled in the liquid condition from T_2 to T_0, and then at this temperature let the part μ_0 be transformed into steam; the piston receding so far, that this steam can again occupy its original space.

Thus the mass $M+\mu$ will have passed through a complete cyclical process, to which we may now apply the principle that the sum of all the quantities of heat taken in during a cyclical process must be equal to the total external work done. In this case the following quantities of heat have been taken in:

(1) In the boiler, where the mass M has been heated from T_2 to T_1, and at the latter temperature the part m_1 transformed into steam, we have the quantity of heat

$$m_1\rho_1 + MC(T_1 - T_2).$$

(2) During the condensation of m_2 at temperature T_2, we have

$$-m_2\rho_2.$$

(3) During the cooling of the part μ from T_2 to T_0, we have

$$-\mu C(T_2 - T_0).$$

(4) During the vaporization of the part μ_0 at temperature T_0, we have

$$\mu_0\rho_0.$$

The whole quantity of heat taken in, which we may call Q, is thus given by

$$Q = m_1\rho_1 - m_2\rho_2 + MC(T_1 - T_2) + \mu_0\rho_0 - \mu C(T_2 - T_0) \ldots (19).$$

The quantities of work are obtained as follows:

(1) To determine the space swept through by the piston during the entrance of the steam, we must remember

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gaseous condition at the end as at the beginning, we need only assume that the water forced back into the boiler is not only in quantity, but also in its actual molecules, the same as that which left the boiler previously; and that when this water takes up the temperature T_1, the quantity m_1 which was formerly vapour, is again vaporized, whilst an equal quantity of the existing steam is condensed. For this purpose there is no need that the whole mass in the boiler should take in or give out any heat, because that required for the vaporization, and that generated by the condensation, exactly balance each other.

that the whole space taken up by $M+\mu$ at the end of this time is given by

$$m_2\mu_2+(M+\mu)\sigma.$$

From this we must subtract the waste space. Since this is filled at the commencement by a mass μ at temperature T_0, of which the part μ_0 is in the condition of steam, it may be represented by

$$\mu_0 u_0+\mu\sigma.$$

If we subtract this expression from the former, and multiply the remainder by the mean pressure p'_1, we obtain for the first part of the work done

$$(m_2 u_2+M\sigma-\mu_0 u_0)\,p_1'.$$

(2) The work done in the condensation of the mass m_2 is

$$-m_2 u_2 p_2.$$

(3) The work done in forcing the mass M back into the boiler is

$$-M\sigma p_1.$$

(4) The work done in vaporizing the part u_0 is

$$\mu_0 u_0 p_0.$$

Adding these four quantities together we obtain the following expression for the whole work done:

$$W=m_2 u_2(p_1'-p_2)-M\sigma(p_1-p_1')-\mu_1 u_0(p_1'-p_0)\ldots\ldots(20).$$

Since $Q=W$, we may equate the expressions in (19) and (20); and bringing to one side of the equation the terms containing m_2, we obtain

$$m_2[\rho_2+u_2(p_1'-p_2)]=m_1\rho_1+MC(T_1-T_2)+\mu_0\rho_0-\mu C(T_2-T_0)$$
$$+\mu_0 u_0(p_1'-p_0)+M\sigma(p_1-p_1')\ldots\ldots\ldots\ldots(21).$$

By means of this equation the quantity m_2 is given in terms of quantities assumed to be already known.

§ 11. *Divergence of the above Results from Pambour's Assumption.*

In cases where the mean pressure p_1' is much larger than the final pressure p_2,—e. g. if we suppose that during the greater part of the time of admission of the steam, the pressure in the cylinder is nearly the same as in the boiler, and that it is only by the expansion that the pressure is finally brought down to the value p_2,—it may happen that the value found for m_2 is less than $m_1 + \mu_0$, and accordingly that a part of the original steam must have condensed. On the other hand if p_1' is only a little greater or even a little smaller than p_2, then the value of m_2 will be greater than $m_1 + \mu_0$. This latter is in general true of the steam-engine, and in particular holds for the case assumed by Pambour, in which $p_1' = p_2$.

Here as in Chapter VI. we have arrived at a result widely diverging from the views of Pambour. Whereas he assumed for the two different kinds of expansion, which succeed each other in the steam-engine, one and the same law, according to which the original quantity of steam can neither grow less nor greater, but must always remain exactly at maximum density, we have been led to two separate equations, which indicate an opposite condition of things. In the first expansion, during the admission of steam, there must by equation (21), be a continual generation of fresh steam; in the further expansion, after the steam is cut off, and while it is doing the full work corresponding to its force of expansion, there must by equation (56) of Chapter VI. be a condensation of some part of the existing steam.

Since these two opposite processes of increase and diminution of steam, which must also exert an opposite influence on the amount of work done by the engine, partly go to cancel each other, the final result may in certain circumstances be nearly the same as under the simpler assumption of Pambour. We must not however on this account cease to take into consideration the difference we have discovered, especially if our object is to determine what effect a change in the arrangement or speed of the engine will have on the amount of work done.

§ 12. *Determination of the Work done during one stroke, taking into consideration the Imperfections already noticed.*

We may now return to the complete cyclical process performed by the steam-engine, and treat its several parts one after another in the same way as before.

The mass M flows from the boiler, in which the pressure is p_1, into the cylinder. Of this mass the part m_1 is in the condition of steam, the remainder of water. The mean pressure in the cylinder during this time we will as before call p_1', and the final pressure p_2. The steam now expands, until its pressure has fallen from p_2 to p_3, and its temperature from T_2 to T_3. Then the cylinder is opened to the condenser, the pressure in which is p_0, and the piston moves back again through the whole length of the stroke. The back pressure which it has to overcome is on account of its comparatively rapid motion somewhat larger than p_0, and the mean value of this back pressure we will for the sake of distinction call p_0'. The steam which remains in the waste space at the end of the return stroke, and must be taken into account for the next stroke, has a pressure which may not be equal either to p_0 or to p_0', and therefore must be denoted by p_0''. It may be greater or less than p_0', according as the steam is shut off from the condenser a little before or after the end of the return stroke; for in the former case the steam will be compressed still further, while in the latter it will have time to escape partially into the condenser and so to expand again. Finally the mass M must be returned from the condenser into the boiler, during which as before the pressure p_0 assists the operation, and the pressure p_1 has to be overcome.

The quantities of work done during these processes will be represented by expressions very similar to those in the simpler case already considered: a few obvious changes must be made in the suffixes to the letters, and the quantities added which refer to the waste space. We thus obtain the following equations:

During the admission of steam we have, as in § 10, only writing u_0'' instead of u_0,

$$W_1 = (m_2u_2 + M\sigma - m_0u_0'')\,p_1' \quad \ldots\ldots\ldots\ldots(22).$$

During the expansion from pressure p_2 to p_3, we have as in equation (62) of Chapter VI., writing $M+\mu$ instead of M,

$$W_2 = m_3u_3p_3 - m_2u_2p_2 + m_2\rho_2 - m_3\rho_3 + (M+\mu)\,C\,(T_2 - T_3) \quad \ldots\ldots\ldots(23).$$

During the return stroke of the piston, where the whole space swept through by the piston equals the whole space occupied by $M+\mu$ at pressure p_3, less the waste space which is represented by $\mu_0 u_0'' + \mu\sigma$, we have

$$W_3 = -(m_3 u_3 + M\sigma - \mu_0 u_0'')\, p_0' \ldots\ldots\ldots\ldots (24).$$

During the forcing back of the mass M into the boiler we have

$$W_4 = -M\sigma\,(p_1 - p_2) \ldots\ldots\ldots\ldots\ldots\ldots (25).$$

Hence for the total work done we have

$$\begin{aligned} W' = {} & m_2\rho_2 - m_3\rho_3 + (M+\mu)\; C\,(T_2 - T_1) \\ & + m_2 u_2\,(p_1' - p_2) + m_3 u_3\,(p_3 - p_0') \\ & - M\sigma\,(p_1 - p_1' + p_0' - p_0) - \mu_0 u_0''\,(p_1' - p_0') \ldots (26). \end{aligned}$$

In this equation the masses m_2 and m_3 are given by equation (21) and by equation (55) of Chapter VI. respectively; substituting in the former p_0'' for p_0, and changing T_0, r_0, u_0 in the same way, while in the latter $M+\mu$ is to be substituted for M, ρ for r, and C for c. The elimination of m_1 and m_2 is thus rendered possible: here however we shall only make the substitution in the case of one of them, m_2, as it is more convenient for purposes of calculation to combine the equation so obtained with the two named above. Thus the system of equations serving to determine the work done by the steam-engine will, in its most general form, be as follows:

$$\left.\begin{aligned} W' = {} & m_1\rho_1 - m_3\rho_3 + MC\,(T_1 - T_3) \\ & + \mu_0\rho_0'' - \mu C\,(T_3 - T_0'') + m_3 u_3\,(p_3 - p_0') \\ & + m_2 u_0''\,(p_0' - p_0'') - M\sigma\,(p_0' - p_0) \\ m_2\,[\rho_2 + u_2\,(p_1' - p_2)] = {} & m_1\rho_1 \\ & + MC\,(T_1 - T_2) + \mu_0\rho_0'' - \mu C\,(T_2 - T_0'') \\ & + \mu_0 u_0''\,(p_1' - p_0'') + M\sigma\,(p_1 - p_1') \\ \frac{m_3\rho_3}{T_3} = {} & \frac{m_2\rho_2}{T_2} + (M+\mu)\; C \log\frac{T_2}{T_3} \end{aligned}\right\} \ldots (27).$$

§ 13. *Pressure of Steam in the Cylinder during the different Stages of the Process, and corresponding Simplifications of the Equations.*

To obtain numerical values from equations (27), we must first determine more accurately the quantities p_1', p_0', p_0''.

No general law can be laid down as to the mode in which the pressure within the cylinder varies during the admission of steam, because the opening and closing of the steam pipe is performed with different engines in different ways. For the same reason no fixed general value can be laid down for the relation between the mean pressure p_1' and the final pressure p_2, taking the latter in its strictest meaning. This is however possible if we make a slight change in the signification of p_2.

The shutting off of the cylinder from the boiler cannot of course be instantaneous: the necessary motion of the valve or cock must consume a certain time, less or greater according to the arrangement of the gear. During this time the steam in the cylinder expands somewhat, because as the opening narrows the quantity of fresh steam which enters is less than corresponds to the speed of the piston. We may therefore assume in general that at the end of this time the pressure is already somewhat less than p_1'.

Again, if we do not limit ourselves to taking the end of the time required to close the valve as the moment of cut-off, but allow ourselves some freedom in fixing this moment, other values may be obtained for p_2. The moment may be so chosen that, if at this moment the whole mass M had already been admitted, a pressure would then exist exactly equal to the mean pressure calculated for all the time up to this instant. If we substitute for the actual cut-off the instantaneous cut-off as thus determined, the resulting error in the calculation of the work will be quite insignificant. With this modification therefore we can fall in with Pambour's assumption, that $p_1' = p_2$, but we must then for each particular case make a special investigation of the circumstances, in order to determine accurately the moment to be fixed for the cut-off.

As regards the back-pressure p_0', which exists during the return stroke, the difference $p_0' - p_0$ is obviously smaller, other things being equal, as p_0 is smaller. It is therefore smaller for a condensing engine than for a high-pressure engine, where p_0 equals one atmosphere. In the case of the most important high-pressure engine, the locomotive, there is generally a special circumstance which tends to increase this difference, viz. that the steam is not usually led into the air by the shortest and widest channel possible, but is led into the chimney, and there allowed to escape through a somewhat contracted blast-pipe, in order to increase the draught. In this case an accurate determination of this difference is of importance to obtain a trustworthy result. It must also be remembered that this difference is not constant even with the same engine, but depends upon the speed, and the law of this dependence must therefore be investigated. This subject, with the researches made upon it, will not however be entered on here, since it has nothing to do with the present application of the Mechanical Theory of Heat.

In the case of engines where the exhaust steam is not thus employed, and especially with condensing engines, p_0' differs so little from p_0, and therefore varies so slightly with the speed, that it is usually sufficient to assume a mean value for p_0'. Moreover, since p_0 enters into equations (27) only in terms which are multiplied by σ, and therefore have but small influence on the value of the work done, we may also substitute for p_0 the most probable value for p_0'.

The pressure p_0'', which exists in the waste space, depends, as already mentioned, on whether the shutting off from the condenser takes place before or after the end of the stroke, and may therefore have very different values. But this pressure, and the quantities depending on it, occur in equations (27) only in terms containing the small factors μ and μ_0, so that an approximate value is sufficient for our purpose. In cases where there are no special circumstances which cause p_0'' to vary widely from p_0', we may neglect this difference, as we did that between p_0 and p_0', and may thus assume as a general value for all three quantities the most probable mean value for the back-pressure within the cylinder. This value we may call p_0.

These simplifications change equations (27) into the following:

$$\left.\begin{aligned} W' &= m_1\rho_1 - m_3\rho_3 + MC(T_1 - T_2) + \mu_0\rho_0 - \mu C(T_3 - T_0) \\ &\qquad + m_3u_3(p_3 - p_0) \\ m_2\rho_2 &= m_1\rho_1 + MC(T_1 - T_2) + \mu_0\rho_0 - \mu C(T_2 - T_0) \\ &\qquad + \mu_0u_0(p_2 - p_0) + M\sigma(p_1 - p_2) \\ \frac{m_3\rho_3}{T_3} &= \frac{m_2\rho_2}{T_2} + (M + \mu)\, C \log \frac{T_2}{T_3} \end{aligned}\right\} \quad (28).$$

§ 14. *Substitution of the Volume for the corresponding Temperature in certain cases.*

In the above equations it is assumed that, besides the masses M, m_1, μ, and μ_0, of which the two first must be found by direct observation, and the two latter can be approximately determined from the size of the waste space, we have also given the four pressures p_1, p_2, p_3, and p_0, or, which is the same thing, the four temperatures T_1, T_2, T_3, and T_0. In practice however this condition is only partially fulfilled, and we must therefore bring in other data to assist us.

Of the four pressures here mentioned, two only, p_1 and p_0, may be taken as known: of these the first is given directly by the gauge on the boiler, and the latter can be at least approximately fixed by the gauge on the condenser. The two others, p_2 and p_3, are not given directly; but we know the dimensions of the cylinder and the point of cut-off, and can thence deduce the volume of the steam at the moment of cut-off and at the end of the stroke. We may then take these volumes as our data in place of the pressures p_2 and p_3. For this purpose we must throw the equations into a form, which will enable us to use the above data for calculation.

Let us now, as before in the explanation of Pambour's theory, denote by v' the whole space within the cylinder which is open to the steam during one stroke, including the waste space; by ev' the space opened to the steam up to the moment of cut-off; and by $\epsilon v'$ the waste space. Then in the same way as before we have the following equations:

$$m_2 u_2 + (M + \mu)\,\sigma = ev',$$

$$m_3 u_3 + (M + \mu)\,\sigma = v',$$

$$\mu_0 u_0 + \mu\sigma = \epsilon v'.$$

The quantities μ and σ are both so small that their product may be at once neglected; whence we have

$$\left.\begin{aligned} m_2 u_2 &= ev' - M\sigma \\ m_3 u_3 &= v' \ - M\sigma \\ \mu_0 &= \frac{\epsilon v'}{u_0} \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots(29).$$

Further, we have by equation (13) of Chapter VI.

$$\rho = Tug,$$

writing the single letter g for $\frac{dp}{dT}$, which will occur very frequently in what follows. We can therefore replace ρ_2 and ρ_3 in equations (28) by u_2 and u_3. Then the masses m_2 and m_3 occur only in the products m_2u_2 and m_3u_3, for which we may substitute the values given in the two first of equations (29). Again, by the last of these equations we may eliminate the mass μ_0; and as regards the other mass μ, though this may be somewhat larger than μ_0, yet, since the terms which contain μ are generally insignificant, we can without serious error use the value found for μ_0: in other words we may drop for the purposes of calculation the assumption made for the sake of generality, that the original mass in the waste space is partly liquid and partly gaseous, and consider the whole of it to be in the gaseous form.

The above substitutions may be effected in the more general equations (27), as well as in the simplified equations (28). This substitution presents no difficulty, and we will here confine ourselves to the latter set, in order to have the equations in a form adapted for calculation. With these changes they read as follows:

$$\left.\begin{aligned} W' = m_1\rho_1 + MC(T_1 - T_3) - (v' - M\sigma)(T_3g_3 - p_3 + p_0)& \\ + \epsilon v'\,\frac{\rho_0 - C(T_3 - T_0)}{u_0}& \\ (ev' - M\sigma)\,T_2g_2 = m_1\rho_1 + MC(T_1 - T_2)& \\ + \epsilon v'\left\{\frac{\rho_0 - C(T_2 - T_0)}{u_0} + p_2 - p_0\right\} + M\sigma(p_1 - p_2)& \\ (v' - M\sigma)\,g_3 = (ev' - M\sigma)\,g_2 + \left(M + \frac{\epsilon v'}{u_0}\right)C\log\frac{T_2}{T_3}& \end{aligned}\right\} (30).$$

§ 15. *Work per Unit-Weight of Steam.*

To adapt the above equations, which give the work per stroke or per quantity of steam m_1, to determine the work per unit-weight of steam, we must apply the same method as before in transforming equation (17) into (18): viz. to divide the three equations by m_1, and then put

$$\frac{M}{m_1} = l, \quad \frac{v'}{m_1} = V, \text{ and } \frac{W'}{m_1} = W;$$

then the equations become

$$\left.\begin{array}{l} W = \rho_1 + lC(T_1 - T_3) - (V - l\sigma)(T_3 g_3 - p_3 + p_0) \\ \qquad\qquad\qquad\qquad\qquad + \epsilon V \dfrac{\rho_0 - C(T_3 - T_0)}{u_0} \\ (eV - l\sigma)\, T_2 g_2 = \rho_1 + lC(T_1 - T_2) \\ \qquad + \epsilon V \left\{ \dfrac{\rho_0 - C(T_2 - T_0)}{u_0} + p_2 - p_0 \right\} + l\sigma(p_1 - p_2) \\ (V - l\sigma)\, g_3 = (eV - l\sigma)\, g_2 + \left(l + \dfrac{\epsilon V}{u_0} \right) C \log \dfrac{T_2}{T_3} \end{array}\right\} (31).$$

§ 16. *Treatment of the Equations.*

The application of the above equations to calculate the work done may be effected as follows. Assuming the pressure of steam to be known, and also the speed at which the engine works, we can thence determine the volume V of one unit-weight of steam. By help of this value we first calculate the temperature T_2 from the second equation, then T_3 from the third, and finally apply these to determine the work done from the first equation.

Here however we are met by another difficulty. In order to calculate T_2 and T_3 from the two latter equations, these must be solved for those temperatures. But they contain those temperatures not only explicitly but also implicitly, since p and g are functions of temperature. If to eliminate these quantities we use for p one of the ordinary empirical expressions for the pressure as a function of temperature, and for g the differential coefficient of the same expression, then the equations become too complicated for further treatment. It would probably be possible to adopt the same method as Pambour, and to form new empirical formulæ, more convenient for the present purpose, and sufficiently accurate, if not for all temperatures at least within certain limits. This however will not here be attempted, but another method will be adopted instead, which makes the calculation somewhat extended, but easily performed in its individual parts.

§ 17. *Determination of* $\frac{dp}{dt}$ *or* g, *and of the Product* Tg.

If the range of pressure of the vapour at different temperatures is known with sufficient accuracy for any liquid, then the values of g and Tg can also be calculated for the same temperatures, and collected in tables, as usually done with the values of p. For steam, which has hitherto been the only vapour used for the steam-engine, the author has performed such a calculation, by help of Regnault's tables, for temperatures from 0° to 200°. For this purpose he differentiated according to t the formula used by Regnault to calculate the values of p under and above 100°; and then calculated g by means of the new formulæ thus obtained. But since these formulæ did not seem to answer the purpose so well as to repay the great labour involved, and since the forming and calculating of other more suitable formulæ proved still more tedious, the author was contented to use the numbers already calculated for the pressure to determine approximately the differential coefficient of that pressure: e.g., if the pressure for the temperatures 146° and 148° were denoted by p_{146} and p_{148}, it was assumed that $\frac{p_{148}-p_{146}}{2}$ would represent with sufficient accuracy the value of the differential coefficient for the mean temperature 147°.

Above 100° the same numbers were employed as were used by Regnault*. With regard to values under 100° it has been recently pointed out by Moritz† that the formula used by Regnault is somewhat inaccurate, especially in the neighbourhood of 100°, owing to his having employed for the calculation of the constants logarithms to seven places of decimals only. Moritz has therefore recalculated these constants from the same observed values, but using ten places of logarithms, and has published the values of p derived from this improved formula, so far as they differ from Regnault's values, which first takes place at 40°. These are the values used by the author*.

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* *Mém. de l'Acad. des Sciences*, Vol. XXI. p. 625.

† *Bulletin de la Classe physico-mathématique de l'Acad. de St Pétersbourg.* Vol. XIII. p. 41.

When g has been calculated for the various temperatures, the product Tg can be calculated without further difficulty, since T is given by the simple equation

$$T = 273 + t.$$

The values of g and Tg thus found are given in a table at the end of this Chapter. To complete this the corresponding values of p are added, those from 0° to 40° and above 100° being Regnault's numbers, and those from 40° to 100° being Moritz's. By the side of each of these three columns are given the differences between each two successive numbers, so that this table enables the values of these three quantities to be found for any given temperature, and conversely the temperature corresponding to any given value of one of these three quantities.

§ 18. *Introduction of other Measures of Pressure and Heat.*

One other remark is to be made as to the mode of using this table. In equations (31) it is assumed that the pressure p and its differential coefficient g are expressed in kilograms per square metre, whereas in the table the same unit of pressure is employed as in Regnault's tables, viz. a millimetre of mercury. Hence, if in the formulæ which follow we are to consider p and g as expressed in these latter units, we must alter equations (31) by multiplying p and g by the number 13·596 which expresses the specific weight of mercury; inasmuch as this, by Chapter VI., § 10, is the ratio between the units. If we denote this number by k, we must substitute kp and kg for p and g, whenever these occur in the above equations. Similarly for the quantities C and ρ, which express the specific heat and the heat of vaporization in mechanical units, we will use c and r which refer to the ordinary unit of heat. For this purpose we must write Ee and Er for C and ρ.

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* See note at end of chapter.

If we now divide the equations by k, so as to bring the constants E and k together as much as possible, these equations take the following form, from which to calculate $\frac{W}{k}$, and thereby obtain W, the work done:—

$$\left.\begin{aligned}
\frac{W}{k} &= \frac{E}{k}\left[r_1 + lc\,(T_1 - T_3)\right] - (V - l\sigma)\,(T_3 g_3 - p_3 + p_0) \\
&\qquad + \epsilon V \frac{E}{k} \times \frac{r_0 - c\,(T_3 - T_0)}{u_0} \\
(eV - l\sigma)\,T_2 g_2 &= \frac{E}{k}\left[r_1 + lc\,(T_1 - T_2)\right] \\
&\quad + \epsilon V \left\{\frac{E}{k} \times \frac{r_0 - c\,(T_2 - T_0)}{u_0} + p_2 - p_0\right\} + l\sigma\,(p_1 - p_2) \\
(V - l\sigma)\,g_3 &= (eV - l\sigma)\,g_2 + \left(l + \frac{\epsilon V}{u_0}\right)\frac{Ec}{k}\log\frac{T_2}{T_3}
\end{aligned}\right\} \quad (32).$$

The quantity $\frac{E}{k}$ has the following value:

$$\frac{E}{k} = \frac{423{\cdot}55}{13{\cdot}596} = 31{\cdot}1525 \ldots\ldots\ldots\ldots\ldots (33).$$

§ 19. *Determination of the Temperatures* T_2 *and* T_3.

The second of equations (32) may be written as follows:

$$T_2 g_2 = C + a\,(t_1 - t_2) - b\,(p_1 - p_2) \ldots\ldots\ldots\ldots (34),$$

where C, a and b are independent of T_2, and have the values

$$\left.\begin{aligned}
C &= \frac{1}{eV - l\sigma}\left[\frac{Er_1}{k} + \epsilon V\left\{\frac{E}{k} \times \frac{r_0 - c(T_1 - T_0)}{u_0} + p_1 - p_0\right\}\right] \\
a &= \frac{E}{k} \times \frac{c\left(l + \frac{\epsilon V}{u_0}\right)}{eV - l\sigma} \\
b &= \frac{\epsilon V - l\sigma}{eV - l\sigma}.
\end{aligned}\right\} \quad (34a).$$

Of the three terms on the right-hand side of (34) the first is by far the most important; and it is thus possible to determine T_2g_2, and thereby also the temperature t_2, by successive approximations. To obtain the first approximation to Tg, which we may call $T'g'$, we may write t_1 for t_2, and p_1 for p_2. Then we have

$$T'g' = C \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (35).$$

The temperature t' corresponding to this value of Tg must be found from the table. Then to obtain the second approximation to Tg we may write the value t' thus found for t_2 in equation (34), and the corresponding value p' of the pressure for p_2. Thus, remembering equation (35), we have for the second approximation

$$T''g'' = T'g' + a\,(t_1 - t') - b\,(p_1 - p') \ldots\ldots\ldots (35a).$$

The temperature t'' corresponding to this value of Tg must be found as before from the table. If a second approximation be not sufficient, the process must be repeated. Writing in equation (34) t'' and p'' in the place of t_2 and p_2, and remembering equations (35) and (35*a*), we have

$$T'''g''' = T''g'' + a\,(t' - t'') - b\,(p' - p'') \ldots\ldots (35b).$$

The new temperature t''' can again be found from the table.

In this way we may proceed to any degree of approximation; but the third approximation only differs by about $\frac{1}{100}$ of a degree, and the fourth by less than $\frac{1}{1000}$ of a degree, from the true value of t_2.

The treatment of the third of equations (32) is very similar. If we divide by $V - l\sigma$, and for convenience of calculation replace the natural by common logarithms (for which purpose we have to divide by the modulus M) the equation takes the form

$$g_3 = C + a \operatorname{Log} \frac{T_2}{T_3} \ldots\ldots\ldots\ldots\ldots\ldots (36),$$

where C and a have the following values independent of T_3:

$$\left.\begin{aligned} C &= \frac{eV - l\sigma}{V - l\sigma} \times g_2 \\ a &= \frac{E}{k} \times \frac{c\left(l + \dfrac{\epsilon V}{u_0}\right)}{M\,(V - l\sigma)} \end{aligned}\right\} \ldots\ldots\ldots\ldots (36a).$$

In equation (36) the first term is again the most important, and we can therefore proceed by successive approximations. First write T_2 for T_3; we then have as the first approximation for g_3,

$$g' = C \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(37).$$

The corresponding temperature t' can be found from the table, and from this we can easily obtain the absolute temperature T'. Write T' for T_3 in equation (36); then we have

$$g'' = g' + a \operatorname{Log} \frac{T_2}{T'} \quad\ldots\ldots\ldots\ldots\ldots\ldots(37a).$$

This gives T''. Similarly we can obtain the equation

$$g''' = g'' + a \log \frac{T'}{T''} \quad\ldots\ldots\ldots\ldots\ldots\ldots(37b),$$

which again gives T'''; and so on. Here again a very few approximations will give a value which very closely agrees with the actual value of T_3.

§ 20. *Determination of* c *and* r.

It now only remains to determine the quantities c and r, before proceeding to the numerical application of equations (32).

The quantity c, or the specific heat of the liquid, has hitherto been treated as constant. This is not perfectly correct, since it increases slightly as the temperature increases. If however we take as its general value the correct value for the mean of the temperatures which occur in the investigation, the divergencies may be neglected. This mean temperature in the case of engines driven by steam may be taken at 100°, which for an ordinary high-pressure condensing engine is about a mean between the temperature of the boiler and that of the condenser. Taking therefore the value of the specific heat which Regnault gives for water at 100°, we may put

$$c = 1{\cdot}013 \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(38).$$

To determine r we start from the equation which Regnault gives for the whole quantity of heat required to heat a unit-weight of water from 0° to the temperature t, and to transform it at that temperature into steam. This equation is

$$\lambda = 606{\cdot}5 + 0{\cdot}305t.$$

If here we substitute for λ the expression corresponding to the foregoing definition, viz. $\int_0^t cdt + r$, we have

$$r = 606{\cdot}5 + 0{\cdot}305t - \int_0^t cdt.$$

In the integral we must use for c the function of temperature exactly determined by Regnault*, if we are to obtain for r the precise values which Regnault gives. For the present purpose it is perhaps sufficient here also to use for c the constant above-mentioned. This gives

$$\int_0^t cdt = 1{\cdot}013t;$$

and the two terms involving t in the last equation can now be combined into one, viz. $-0{\cdot}708t$. We must at the same time make some change in the constant term of the equation. This we will so determine, that the same value of r which is probably the most accurate of all given by observation, shall also be correct as given by the formula. Now at 100° Regnault found for λ, as the mean of 38 observations, the value 636·67. If from this we subtract the quantity of heat required to heat the unit-weight of water from 0° to 100°, which according to Regnault is 100·5 heat-units, there remains to one place of decimals only

$$r_{100} = 536{\cdot}2\dagger.$$

Applying this value we obtain for r the formula

$$r = 607 - 0{\cdot}708t \;\ldots\ldots\ldots\ldots\ldots\ldots \;(39).$$

This formula is already laid down in Chapter VII., § 3; and a short table is there given, which exhibits the close accordance between the values of r as calculated by this formula, and as given by Regnault in his tables.

§ 21. *Special Form of Equation* (32) *for an Engine working without expansion.*

In order to distinguish the effects of the two different kinds of expansive action, to which the two latter of equations (32) refer, it seems desirable first to consider an engine in which only one of the two occurs. We will therefore begin with an engine that works without expansion. In this case we may substitute for *e*, or the ratio of the volumes before and after expansion, the value 1; and may also put $T_3 = T_2$. The equations (32) are thus greatly simplified. The last becomes an identity, and is therefore useless. In the second the right-hand side remains unaltered, whilst the left-hand side becomes $(V - l\sigma)\,T_2 g_2$. Finally the first equation takes the form

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* *Relation des expériences*, Vol. I. p. 748.

† Regnault himself used in his tables the number 536·5 instead of the above; this simply arises from the fact that he has used the round number 637 for λ at 100°, instead of 636·67 as given above.

$$\frac{W}{k} = \frac{E}{k}\{r_1 + lc\,(T_1 - T_2)\} - (V - l\sigma)\,(T_2 g_2 - p_2 + p_0) \\ + \epsilon V \frac{E}{k} \times \frac{r_0 - c\,(T_2 - T_0)}{u_0}.$$

If we here replace $(V - l\sigma)\,T_2 g_2$ by the expression on the right-hand side of the second equation, all the terms containing $\frac{E}{k}$ as factor cancel each other, as do two terms containing $l\sigma$ as factor, and the terms which remain can be collected together as two products. Then the two equations are

$$\left.\begin{aligned} \frac{W}{k} &= V\,(1 - \epsilon)\,(p_2 - p_0) - l\sigma\,(p_1 - p_0) \\ (V - l\sigma)\,T_2 g_2 &= \frac{E}{k}\{r_1 + lc\,(T_1 - T_2)\} \\ &\quad + \epsilon V \left\{\frac{E}{k} \times \frac{r_0 - c\,(T_2 - T_0)}{u_0} + p_2 - p_0\right\} + l\sigma\,(p_1 - p_2) \end{aligned}\right\} (40).$$

The first of these equations is exactly the same as is given by Pambour's theory, if in equation (18) we put $e = 1$, and then by means of equation (12) (having first put $e = 1$ and $\frac{v'}{m} = V$ in that equation) replace B by the volume V. The only difference therefore is in the second equation, which replaces the simple relation between volume and pressure assumed by Pambour.

§ 22. *Numerical Values of the Constants.*

The quantity ϵ which occurs in these equations, and represents the ratio of the waste space to the whole space left open to the steam, may be taken as 0·05. The quantity of water which the steam carries over with it into the cylinder is different in different engines. Pambour considers that it averages 0·25 of the whole mass entering the cylinder in the case of locomotives, but much less, 0·05, in the case of stationary engines. We will here take the latter value, which gives 1 : 0·95 as the ratio of the whole mass entering the cylinder to that part of it which is in the form of steam. Further, let the pressure in the boiler, or p_1, be five atmospheres, to which corresponds the temperature 152·22°; and let it be supposed that the engine has no condenser, or, which is the same thing, a condenser at the pressure of one atmosphere. The mean back-pressure in the cylinder is then greater than one atmosphere. With locomotives this excess of back-pressure may be considerable, for the special reasons already mentioned; with stationary engines it is insignificant. Pambour, in his tables for stationary non-condensing engines, has altogether neglected this excess; and since our present object is to compare the new formula with his, we will follow his example and put $p_0 =$ one atmosphere.

We have then in this case the following values to insert in equations (40):

$$\left.\begin{aligned} \epsilon &= 0{\cdot}05 \\ l &= \frac{1}{0{\cdot}95} = 1{\cdot}053 \\ p_1 &= 3800 \\ p_0 &= 760 \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots(41).$$

We may also fix once for all the following values:

$$k = 13{\cdot}596,$$

$$\sigma = 0{\cdot}001.$$

There now remain only the quantities V and p_2 undetermined in equations (40), in addition to the quantity W, of which we are seeking the value. Of these V is the volume of steam in the cylinder per unit-weight, and p_2 is the final pressure within the cylinder.

§ 23. *The least possible Value of* V, *and the corresponding amount of Work.*

We must first enquire what is the least possible value of V. This value corresponds to the case in which the pressure in the cylinder is the same as in the boiler, and we have therefore only to substitute p_1 for p_2 in the last of equations (40). Thus we obtain

$$V = \frac{\frac{Er_1}{k} + l\sigma \times T_1 g_1}{T_1 g_1 - \epsilon\left\{\frac{E}{k} \times \frac{r_0 - c\,(T_1 - T_0)}{u_0} + p_1 - p_0\right\}} \quad \ldots(42).$$

In order to give an example of the influence of the waste space, two values have been calculated from this expression; the first that which would exist if there were no waste space, and therefore $\epsilon = 0$; the second that which exists upon our assumption that $\epsilon = 0{\cdot}05$. These two values expressed in cubic metres per kilogram of steam passing out of the boiler are 0·3637 and 0·3690.

The reason why the second value is greater than the first is that the steam rushes at first into the waste space with great velocity; the *vis viva* of this motion is then transformed into heat, and this heat again evaporates some part of the priming water. A second reason is that the steam already existing in the waste space before the admission goes to increase the whole quantity of steam during the rest of the process.

If we substitute these two values of V in the first of equations (40), at the same time putting $\epsilon = 0$ in the one case, and $\epsilon = 0{\cdot}05$ in the other, the corresponding quantities of work, expressed in kilogrammetres, are respectively 14990 and 14450.

According to Pambour's theory it makes no difference with regard to the volume, whether part of it is waste space or not; in both cases it is given by the same equation (11*b*), if for p is substituted the special value p_1. The value thus obtained for the volume is 0·3883. The fact that this value is greater than the value 0·3637 found above for the same quantity of steam, is explained by the circumstance that it has been until now usual to assume for steam at its maximum density a volume greater than is allowed by the mechanical theory of heat; this view finds its expression in equation (11*b*). If by means of this latter volume we determine the work from Pambour's equation upon the two assumptions that $\epsilon = 0$ and that $\epsilon = 0{\cdot}05$, the values obtained are 16000 and 15200. These quantities, as follows immediately from the greater volume, are both greater than those found above, but not in the same ratio, because the loss of steam due to the waste space is smaller according to our equations than according to Pambour's theory.

§ 24. *Calculation of the Work for other Values of* V.

With an engine of the kind here considered, the efficiency of which was investigated by Pambour, the speed which the engine actually assumed bore a proportion in one case of 1·275 : 1, and in another, with a lighter load, of 1·70 : 1, to the minimum speed as calculated by his theory for the same intensity of evaporation, and for the same boiler-pressure. To these speeds correspond in our case the volumes 0·495 and 0·660 respectively. We will now, as an example of the mode of determining the work done, choose a speed which lies between these two, say in round numbers

$$V = 0{\cdot}6.$$

Our first business is now to find the value of T_2 corresponding to this value of V. For this purpose we use equation (34), which takes the following special form:

$$T_2 g_2 = 26{\cdot}577 + 56{\cdot}42\,(t_1 - t_2) - 0{\cdot}0483\,(p_1 - p_2) \quad \ldots(43).$$

If by means of this equation we obtain successive approximations to t_2, as described in section (19), the series of values is as follows:

$$t' = 133{\cdot}01,$$
$$t'' = 134{\cdot}43,$$
$$t''' = 134{\cdot}32,$$
$$t'''' = 134{\cdot}33.$$

Further approximations would differ only in higher places of decimals, and if we confine ourselves to two places we may take the last number as the true value of t_2. The corresponding pressure is

$$p_2 = 2308{\cdot}30.$$

If we substitute in the first of equations (40) these values of V and p_2, together with the approximate values of constants as fixed in § 22, we obtain

$$W = 11960.$$

By Pambour's equation (18) we have for the same volume 0·6

$$W = 12520.$$

In order to exhibit more clearly the dependence of the work upon the volume, and at the same time the divergence between Pambour's theory and the author's on this point, calculations similar to that for volume 0·6 have been made for a series of other volumes increasing by equal intervals. The results are given in the following table. The first horizontal row of numbers, which is separated from the rest, contains the values for an engine without waste space. The further arrangement of the table is easily understood.

V	t_2	W	Pambour's Values	
			V	W
0·3637	152·22°	14 990	0·3883	16 000
0·3690	152·22°	14 450	0·3883	15 200
0·4	149·12	14 100	0·4	15 050
0·5	140·83	13 020	0·5	13 780
0·6	134·33	11 960	0·6	12 520
0·7	129·03	10 910	0·7	11 250
0·8	124·55	9 880	0·8	9 980
0·9	120·72	8 860	0·9	8 710
1	117·36	7 840	1	7 440

It will be seen that the quantities of work, when calculated by Pambour's theory, decrease more rapidly as the volume increases than when calculated by the author's; so that whilst at first they are considerably the larger they get nearer and nearer to the latter and finally become smaller. The explanation is that by Pambour's theory, whilst the expansion is going on during the admission, the amount of steam remains always the same as it was at the commencement; while, according to the author's theory, a part of the priming water is afterwards evaporated, and this quantity is greater the greater the expansion.

§ 25. *Work done for a given Value of V by an Engine working with Expansion.*

We will now treat in the same way an engine working with expansion, and will choose as our example a condensing engine. To fix the degree of expansion, we will assume that the steam is cut off at one third of the stroke. We then have, to determine e, the equation

$$e - \epsilon = \tfrac{1}{3}(1 - \epsilon);$$

whence, giving to ϵ the value 0·05, we have

$$e = \frac{1 \cdot 1}{3} = 0 \cdot 3666.$$

Let the boiler-pressure be as before five atmospheres. The condenser-pressure can with good arrangements be kept below $\frac{1}{10}$ atmosphere. But since it is not always so small, and in addition the back-pressure in the cylinder somewhat exceeds the pressure in the condenser, we will assume the mean back-pressure p_0 to be in round numbers $\frac{1}{5}$ atmosphere, or 152 millimetres. To this corresponds the temperature $t_0 = 60 \cdot 46^\circ$. If lastly we give to l the same value as before, the constants to be used in our example will be as follows:

$$\left.\begin{aligned} e &= 0 \cdot 36667 \\ \epsilon &= 0 \cdot 05 \\ l &= 1 \cdot 053 \\ p_1 &= 3800 \\ p_0 &= 152 \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (44).$$

To be able to calculate the work done, we only now need to know the value of V. To assist us in choosing this, we must first know the least possible value of V. This is found exactly as in the case of the engine without expansion, by putting p_1 for p_2 in the second of equations (32), and altering the other magnitudes, which are in combination with p_2, in the same way. We thus obtain in the present case the value 1·010. Starting from this, we will first suppose that the actual speed of the engine exceeds the least possible in the ratio 3 : 2. We may then put in round numbers $V=1{\cdot}5$, and we will calculate the work done at this speed.

We first determine the two temperatures t_2 and t_3, by substituting this value of V in the two last of equations (32). Of these t_2 has already been approximately found for the non-condensing engine; and since the present case only differs from the former inasmuch as the quantity e, which was there taken equal to 1, has here a different value, we need not go through the process again, but will merely give the final result, which is

$$t_2 = 137{\cdot}43^\circ.$$

To determine t_3 we have equation (36), which takes in this case the form

$$g_3 = 26{\cdot}604 + 51{\cdot}515 \operatorname{Log} \frac{T_2}{T_3} \ldots\ldots\ldots\ldots\ldots (45).$$

From this we obtain the following successive approximations:

$$\left.\begin{aligned} t' &= 99{\cdot}24^\circ \\ t'' &= 101{\cdot}93 \\ t''' &= 101{\cdot}74 \\ t'''' &= 101{\cdot}76 \end{aligned}\right\}.$$

The last of these, from which further approximations would only diverge in higher places of decimals, we will consider to be the correct value of t_3, and will apply it, together with the known values of t_1 and t_0, to the first of equations (32). Thus we obtain

$$W = 31080.$$

If, taking the same value for V, we calculate the work done by Pambour's equation (18), remembering to determine B and b not from equation (11b) as with the non-condensing engine, but from equation (11a) which refers to condensing engines, we find

$$W = 32640.$$

§ 26. *Summary of Various Cases relating to the Working of the Engine.*

The work done for the volumes 1·2, 1·8 and 2·1 has been calculated in the same way as described above for the volume 1·5. Further, in order to make clear by an example the influence, which the different imperfections of an engine have upon the amount of the work done, the following cases are subjoined.

(1) The case of an engine which has no waste space, and in which the cylinder pressure is equal to the boiler pressure, and the expansion carried so far that the pressure has fallen from its original value p_1 to p_0. If we only assume further that p_0 is exactly equal to the condenser pressure, this case is that to which equation (9) relates, and which gives the greatest possible amount of work for a given quantity of heat, when the temperatures at which the heat is taken in and given off are also given.

(2) The case of an engine, where there is again no waste space, and the cylinder and boiler-pressures are equal, but where the expansion is not as before complete, but is only in the proportion of $e : 1$. This is the case to which equation (6) refers; except that there, in order to determine the magnitude of the expansion, the change of temperature in the steam caused thereby was assumed to be known, whereas here the expansion is fixed by the volume, and the change of temperature must be calculated therefrom.

(3) The case of an engine having waste space and incomplete expansion, in which the only one of the above favourable conditions which remains is the fact that the steam in the cylinder has during admission the same pressure as in the boiler, so that the volume has its least possible value. To this are appended the cases already mentioned, in which this last favourable condition is also absent, and the volume has some other given value instead of the least possible.

For purposes of comparison Pambour's theory has also been applied to all these cases except the first, for which equations (11*a*) and (11*b*) do not hold, inasmuch as even the equation which he has determined for low pressures can only be applied to $\frac{1}{2}$ or at the lowest $\frac{1}{3}$ of an atmosphere, whereas here the pressure has to descend to $\frac{1}{5}$ of an atmosphere. For this first case the numerical values given by our equations are as follows:

Volume before expansion = 0·3637,
„ after „ = 6·345,
Work done.................. = 50460.

The result for all the other cases are contained in the following table; in which a line is drawn between the values for an engine without waste space and the remaining values. For the volume are given only the values after expansion, because those before expansion can be at once derived from these by diminishing them in the ratio 1 : *e* or 1 : 0·36667.

V	t_2	t_3	W	Pambour's Values	
				V	W
0·992	152·22°	113·71°	34300	1·032	36650
1·010	152·22°	113·68°	32430	1·032	34090
1·2	145·63	108·38	31870	1·2	33570
1·5	137·43	101·76	31080	1·5	32640
1·8	131·02	96·55	30280	1·8	31710
2·1	125·79	92·30	29490	2·1	30780

§ 27. *Work done per Unit of Heat delivered from the source of heat.*

The quantities of work done, as given in the above table, and in the previous table for non-condensing engines, are calculated per kilogram of steam received from the boiler. It is easy to deduce from this the quantity of work done per unit of heat delivered from the source of heat, if we remember that for each kilogram of steam so much heat must be delivered, as is necessary to raise the mass *l*, which is somewhat greater than one kilogram, from the initial temperature, at which it enters the boiler, to the boiler temperature itself, and transform it at this latter temperature into steam. This quantity of heat can be calculated from the data already given.

§ 28. *Friction.*

Something must be said in conclusion on the subject of friction. This will be confined to a justification of the course adopted in leaving friction altogether out of account in the equations hitherto developed. For this purpose we will shew that instead of introducing friction at once into the first general expressions for the work, as Pambour has done, the same principles will allow us to take it into account subsequently, according to the method already adopted by other authors.

The forces which the engine has to overcome during its stroke may be distinguished as follows: (1) The resistance which it meets with from without, and in overcoming which consists its useful work. Pambour has named this the load (*charge*) of the engine. (2) The resistances which originate within the machine itself, so that the work expended in overcoming them produces no useful effect. These latter resistances we combine under the name of Friction, although in strictness they comprise other forces than those of friction, especially the resistances of the various pumps driven by the engine, with the exception of the feed-pump, the effect of which has already been considered.

Both these kinds of resistances Pambour takes into account as forces which oppose the motion of the piston; and in order to be able to combine them readily with the pressures of the steam on both sides of the piston, he made his method of denotation agree with that used in the case of the steam pressures, so that the symbol denotes not the whole force, but the force referred to one unit of surface of the piston. On this understanding let the load be represented by R.

A yet further distinction must be made with regard to the friction. This has not the same constant value for any one engine, but increases with the load. Pambour divides it therefore into two parts, that which exists when the engine runs unloaded and that which is brought into action by the load. The latter he takes to be proportional to the load itself. He accordingly expresses the friction per unit of surface by $f + \delta R$, where f and δ are quantities which depend on the construction and dimensions of the engine, but for any one engine may according to Pambour be considered as constant.

We may now refer the work done by the engine to these resisting forces, instead, as hitherto, to the moving force of the steam. The negative work done by the former must equal the positive work done by the latter, because otherwise an acceleration or retardation of the speed would take place, and this is against our original assumption that the speed is uniform. Whilst one unit-weight of steam enters the cylinder, the piston passes through the space $(1-\epsilon)\,V$, and we thus obtain the following expression for the work W:

$$W = (1-\epsilon)\,V\,[(1+\delta)\,R + f].$$

The useful part of this work, which for distinction we may call (W), is expressed as follows:

$$(W) = (1-\epsilon)\,V \times R.$$

If we eliminate R from this equation by means of the one above, we obtain

$$(W) = \frac{W-(1-\epsilon)\,Vf}{1+\delta} \quad\ldots\ldots\ldots\ldots\ldots (46).$$

By help of this equation, since V is assumed to be known, we can deduce the useful work (W) from the whole work W, as soon as f and δ are given us. The manner in which these are determined by Pambour will not be entered upon here, since that determination rests upon insecure grounds, and friction is not the special subject of this chapter.

§ 29. *General Investigation of the Action of Thermodynamic Engines and of its Relation to a Cyclical Process.*

We have now so far completed our treatment of the steam-engine, that we have followed out all the processes which take place, determined the several positive or negative quantities of work performed therein, and combined these into one algebraic expression. We will proceed to consider thermo-dynamic engines from a more general point of view. The expression that an engine is driven by heat must not of course be understood of the direct action of the heat, but only that some substance within the engine sets the working parts in motion through the changes which it undergoes by means of heat. This substance we will call the transmitter of the heat's action.

If a continuously working engine is at uniform speed, all the changes which occur must be periodic, so that the same condition in which the engine and all its parts may be found at any given time, will recur at regular intervals. Therefore the substance transmitting the heat's action must also at such recurring moments exist within the engine in the same quantity and under the same conditions. This may be accomplished in two different ways. (1) The same original quantity of this substance may always remain within the engine; in which case the changes which it undergoes during the motion must be such, that at the end of each period it returns to its original condition, and the same cycle of changes then begins anew. (2) The engine may get rid at the end of each period of the substance which during that period has served to produce its action, and may then take in the same quantity of the same substance from without.

This latter method is the more usual in practice. It exists, e.g. in the hot-air engine, as hitherto constructed, since after every stroke the air which has driven the piston in the working cylinder passes out into the atmosphere, and is replaced by an equal quantity of air drawn from the atmosphere by the feeding cylinder. The same is the case with the non-condensing steam-engine, in which the steam passes from the cylinder into the atmosphere, and is replaced by fresh water, pumped from a reservoir into the boiler. It also applies, partially at least, to the ordinary condensing steam-engine. In this the condensed water is indeed in part pumped back into the boiler, but not as a whole, because it mixes with the cold water, a part of which also enters the boiler. The part of the condensed water which is not used again, together with the remainder of the cold water, must go to waste.

The first method has hitherto been applied in a few engines only, amongst others in engines driven by two different vapours, e.g. steam and ether*. In these the steam is condensed by contact with metal pipes filled inside with liquid ether, and is then wholly pumped back into the boiler. Similarly the ether vapour is condensed in metal pipes surrounded by cold water, and is then pumped back into the vessel used for evaporating the ether. To keep up a uniform working, it is therefore necessary merely to add so much water and ether as is lost by leakage.

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* *Annales des Mines*, 1853, pp. 203, 281.

In an engine of this kind, in which the same mass of vapour is continually used anew, the different changes which this mass undergoes during each period must, as shewn above, form a complete circuit, or in the terms of this treatise a cyclical process. On the contrary the engines in which a periodical admission and emission of vapour takes place are not necessarily subject to this condition. Nevertheless they may fulfil it, provided that they emit the vapour in the same condition in which they received it. This is the case with a condensing steam-engine, in which the steam passes away from the condenser as water and at the same temperature at which it passed from the condenser into the boiler. The waste water, which enters the condenser cold and leaves it hot, need not be taken into account, because it does not appertain to the substance transmitting the heat's action, but merely serves as a negative source of heat.

With other engines the conditions at the emission and admission are different. For example, hot-air engines, even if fitted with a regenerator, send the air back to the atmosphere at a higher temperature than that at which it enters; and non-condensing engines take in water and emit steam. In these cases no complete cyclical process takes place; but it is always possible to conceive that the actual engine has another attached to it, which receives the vapour from the first, restores it in some way to its original condition, and then lets it escape. The two can then be considered as one engine satisfying the above condition. In many cases the process can be completed in this way, without making the investigation too complicated; e.g. we may suppose that a non-condensing steam-engine, assuming that the feed water is at 100°, is replaced by an engine having a condenser, the temperature of which is 100°.

We may thus apply to all thermo-dynamic engines the principles which hold for a cyclical process, if we only suppose those engines which do not of themselves fulfil the condition, to be completed in the manner described: and we can thereby arrive at certain conclusions which are independent of the special nature of the process in each particular engine.

§ 30. *Equations for the Work done during any Cyclical Process.*

For any cyclical process the two equations hold which have been previously developed (Chs. II. and IV.) as analytical expressions of the two fundamental principles, provided the second is further extended so as to embrace non-reversible changes. These equations are

$$\left.\begin{aligned} W &= Q, \\ \int\frac{dQ}{T} &= -N \end{aligned}\right\} \qquad \text{.....................}(47),$$

where N denotes the uncompensated transformation occurring during the process, which is always positive, and has for reversible processes the limiting value zero.

If we apply these equations to the cyclical process which takes place during a period of the thermo-dynamic engine, we see at once that if the whole quantity of heat taken in by the substance transmitting the heat's action is given, then the work also is immediately given by the first equation, without our needing to know the nature of the process itself. By combining the two equations we may also determine the work from other data in an equally general manner.

We will suppose that the quantities of heat, which the variable body receives successively, and its temperature at the moment of receiving each, are given, with the exception of one temperature T_0, at which the body receives a certain quantity of heat (or if it is negative generates it) the magnitude of which is not at present known. Let Q_1 be the sum of all the known quantities, and let Q_0 be the unknown quantity of heat. Now let us divide the integral in the second of equations (47) into two parts, one of which relates to the known quantity of heat Q_1, and the other to the unknown quantity Q_0. In the latter T has the constant value T_0; it is therefore immediately integrable, and gives the expression

$$\frac{Q_0}{T_0}.$$

The second equation thus becomes

$$\int_0^{Q_1} \frac{dQ}{T} + \frac{Q_0}{T_0} = -N,$$

whence

$$Q_0 = -T_0 \int_0^{Q_1} \frac{dQ}{T} - T_0 N.$$

Again, since $Q = Q_1 + Q_0$, the first equation gives

$$W = Q_1 + Q_0,$$

or, substituting for Q_0 its value just found,

$$W = Q_1 - T_0 \int_0^{Q_1} \frac{dQ}{T} - T_0 N \quad \text{............}(48).$$

If we make the special assumption that the whole process is reversible, then $N = 0$, and the above equation becomes

$$W = Q_1 - T_0 \int_0^{Q_1} \frac{dQ}{T} \quad \text{..............}(49).$$

This equation differs from the former only in the term $-T_0 N$. Since N is always positive, this term must be negative; whence we see, as is easily proved directly, that under the conditions fixed above with respect to the imparting of the heat, the greatest possible amount of work is obtained when the whole cyclical process is reversible; and that every circumstance, which causes the changes in a cyclical process not to be reversible, diminishes the amount of work done.

Equation (48) therefore leads to the required value of the work done in a way which is the exact opposite to the ordinary; for we do not, as in other cases, determine the several quantities of work done during the several changes, and then add them together, but we start from the maximum of work, and then subtract from this the losses of work due to the various imperfections of the process. This method may therefore be called the method of subtraction. If we limit the conditions under which the heat is imparted, by supposing that the whole quantity Q_1 is imparted at a given temperature T_1, then the other part of the integral also becomes immediately integrable, and gives $\frac{Q_1}{T_1}$. Equation (47) then takes the following form for the maximum work:

$$W = Q_1 \frac{T_1 - T_0}{T_1} \quad \text{..................(50)}.$$

§ 31. *Application of the above Equations to the Limiting Case in which the Cyclical Process in a Steam-Engine is Reversible.*

Among the cases considered above with regard to the action of the steam-engine, there is one which cannot indeed be attained in practice, but which it is desirable to approach as nearly as possible, viz. the case in which there is no waste space, in which the cylinder-pressure is the same as in the boiler or condenser respectively, and in which the expansion extends so far, that the steam is thereby cooled from the temperature of the boiler to that of the condenser. In this case the cyclical process is reversible in all its parts. Let us suppose that evaporation takes place in the condenser at the temperature T_0; that a mass M, of which the part m_0 is in the gaseous, and the part $M - m_0$ in the liquid form, passes into the cylinder and drives the piston upwards; that by the fall of the piston the steam is first compressed until its temperature rises to T_1, and then at that temperature forced into the boiler; and that lastly the mass M is again brought out of the boiler in the liquid form into the condenser, by means of the small pump, and there cools to the initial temperature T_0. Here the steam passes through the same series of conditions as before, but in the reverse order. The various quantities of heat are imparted or withdrawn in the opposite sense, but to the same amount and at the same temperature of the mass; and all the quantities of work have the opposite signs and the same numerical values. Hence it follows that in this case there is no uncompensated transformation in the process. We may therefore put $N = 0$ in equation (48), thereby obtaining an equation similar to (49), but in which, for the sake of distinction, we will write W' instead of W, viz.

$$W' = Q_1 - T_0 \int_0^{Q_1} \frac{dQ}{T}.$$

Here Q_1 is in our case the heat imparted within the boiler to the mass M, whereby M is heated as liquid from T_0 to T_1, and then the part m_1 transformed into steam. Hence

$$Q_1 = m_1\rho_1 + MC(T_1 - T_0) \dots\dots\dots\dots\dots (51).$$

To determine $\int_0^{Q_1} \frac{dQ}{T}$ we must consider separately the two quantities contained in Q_1, viz. $MC(T_1 - T_0)$ and $m_1\rho_1$. To integrate for the first of these, let us write the element dQ in the form $MCdT$: then this part of the integral becomes

$$MC\int_{T_0}^{T_1} \frac{dT}{T} = MC \log \frac{T_1}{T_0}.$$

Whilst the latter quantity of heat is being imparted, the temperature remains constant at T_1, and the integral in this case is simply

$$\frac{m_1\rho_1}{T_1}.$$

Substituting these values, the expression for W' becomes

$$W' = m_1\rho_1 + MC(T_1 - T_0) - T_0\left(\frac{m_1\rho_1}{T_1} + MC\log\frac{T_1}{T_0}\right)$$

$$= m_1\rho_1\frac{T_1 - T_0}{T_1} + MC\left(T_1 - T_0 + T_0\log\frac{T_0}{T_1}\right).$$

This is the exact expression given in equation (9), and found in sections 4 and 5 by the successive determination of the several quantities of work done during the cyclical process.

§ 32. *Another Form of the Last Expression.*

It was observed in the last section with reference to equation (51) that the two quantities of heat which make up Q_1, viz. $m_1\rho_1$ and $MC\ (T_1 - T_0)$, must be treated differently in the calculation of the work done; inasmuch as the one is imparted to the substance which transmits the heat's action at a fixed temperature T_1, and the other at temperatures rising continuously from T_0 to T_1. Similarly these two quantities of heat occur also in different forms in the expression for the work, as is more clearly shewn if we write our last equation as follows:

$$W' = m_1\rho_1 \frac{T_1 - T_0}{T_1} + MC(T_1 - T_0)\left(1 + \frac{T_0}{T_1 - T_0}\log\frac{T_0}{T_1}\right)\ldots(52).$$

Here $m_1\rho_1$ is multiplied by the factor

$$\frac{T_1 - T_0}{T_1},$$

which occurs in equation (50), while $MC(T_1 - T_0)$ is multiplied by the factor

$$1 + \frac{T_0}{T_1 - T_0}\log\frac{T_0}{T_1}.$$

In order to compare these factors better with each other, we will throw the latter into another form. If for brevity we write

$$z = \frac{T_1 - T_0}{T_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(53),$$

then

$$\frac{T_0}{T_1 - T_0} = \frac{1 - z}{z}, \quad \frac{T_0}{T_1} = 1 - z,$$

and we thus obtain

$$\begin{aligned} 1 + \frac{T_0}{T_1 - T_0}\log\frac{T_0}{T_1} &= 1 + \frac{1 - z}{z}\log(1 - z) \\ &= 1 - \frac{1 - z}{z}\left(\frac{z}{1} + \frac{z^2}{2} + \frac{z^3}{3} + \text{etc.}\right) \\ &= \frac{z}{1 \times 2} + \frac{z^2}{2 \times 3} + \frac{z^3}{3 \times 4} + \text{etc.} \end{aligned}$$

Equation (52) or (9) thus becomes

$$W' = m_1\rho_1 \times z + MC(T_1 - T_0) \times z\left(\frac{1}{1 \times 2} + \frac{z}{2 \times 3} + \frac{z^2}{3 \times 4} + \text{etc.}\right) \quad \ldots\ldots\ldots (54).$$

The value of the infinite series in the bracket, which makes the difference between the factor of $MC(T_1 - T_0)$ and the factor of $m_1\rho_1$, varies, as is easily shewn, between $\frac{1}{2}$ and 1, whilst z increases from 0 to 1.

§ 33. *Influence of the Temperature of the Source of Heat.*

Since, under the assumptions we have made, the cyclical process passed through periodically by the engine during its motion is reversible in all its parts, as shewn in § 31, and since a reversible process gives the maximum work attainable, we are able to lay down the following principle:—

If the temperatures at which the substance transmitting the heat's action takes in the heat from the source, or gives it out externally, are taken as given beforehand, then the steam-engine, under the assumptions made in the development of equations (9) or (52), is a perfect engine, inasmuch as with a given quantity of heat imparted to it, it performs the greatest quantity of work, which according to the Mechanical Theory of Heat it is possible to perform at those temperatures.

It is otherwise, if we consider these temperatures not as given beforehand, but as a variable element which must be taken into account in our estimate of the engine.

The fact that the water, whilst being heated and evaporated, has a much lower temperature than the fire, and therefore the heat imparted to it passes from a higher temperature to a lower, produces an uncompensated transformation which is not included in N of equation (47), but which greatly diminishes the useful effect of the heat. We see by equation (54) that the work obtained by the steam-engine from the quantity of heat $m_1\rho_1 + MC(T_1 - T_0) = Q_1$, is somewhat less than $Q_1\frac{T_1 - T_0}{T_1}$. But if we assume that the substance transmitting the heat's action could have, throughout the time when it is taking in heat, the same temperature as those parts of the fire which furnish that heat; and if we denote the mean value of this temperature by T', and the temperature at which the heat is given off, as before, by T_0; then under these circumstances the work which it is possible to obtain from the quantity of heat Q_1 will by equation (50) be expressed by $Q_1\frac{T' - T_0}{T'}$. To compare the values of this expression in various cases, let t_0, the condenser temperature, be fixed at 50°, and let us take for the boiler temperatures 110°, 150°, and

180°; the two first of which about correspond to those of the low-pressure and ordinary high-pressure engines, while the last may be considered the limit of temperature, which has as yet been practically attempted for the steam-engine. In these cases $\frac{T_1 - T_0}{T_1}$ has the following values (adding in each case the number 273 to give absolute temperatures):

$$\text{When } T_1 = 110^\circ \quad \frac{T_1 - T_0}{T_1} = 0\cdot157,$$

$$\ldots\ldots\ldots\ldots 150^\circ \ldots\ldots\ldots\ldots 0\cdot236,$$

$$\ldots\ldots\ldots\ldots 180^\circ \ldots\ldots\ldots\ldots 0\cdot287.$$

On the other hand if for example we assume t' at 1000°, the corresponding value of $\frac{T' - T_0}{T'}$ is 0·746.

Hence it is easy to see, as already observed by Carnot and subsequent authors, that in order to get the greatest advantage from engines driven by heat, the most important point is to increase the temperature interval $T' - T_0$. For example the hot-air engine can only be expected to shew a decided advantage over the steam-engine, when the possibility is established of its being worked at decidedly higher temperatures, such as are forbidden to the steam-engine for fear of explosion. The same advantage may however be obtained by the use of superheated steam, since, as soon as the steam is separated from the water, it may be heated with no more risk than a permanent gas. Engines which use the steam in the superheated condition ought to unite many advantages of the steam-engine with those of the air-engine, and may therefore be expected to achieve a practical success much sooner than the latter.

In the class of engines mentioned above, in which besides the water another more volatile substance is used, the interval $T_1 - T_0$ is widened, inasmuch as T_0 is lowered. It has been already suggested that the interval might be widened at the higher limit in the same manner, by adding yet a third liquid less volatile than water. The fire would then directly evaporate the first of the three only; this in condensing would evaporate the second, and this in like manner the third. As far as principle goes this combination would undoubtedly be advantageous; the practical difficulties, which might hinder its being carried out, cannot be conjectured beforehand.

§ 34. *Example of the application of the Method of Subtraction.*

The ordinary steam-engine, besides the imperfection described above, which is inherent in its nature, possesses many other imperfections, which are rather due to its construction in practice: some of these have already been taken into account in our investigations to determine the work done. We will now in conclusion exhibit the method in which, with engines possessing such imperfections, the work done may be determined by the method of subtraction given in § 30. In order that we may not extend this investigation, which is merely an example of the mode of applying this method, to too great a length, we will only take into account two of these imperfections, viz. the existence of the waste space and the difference of the pressures in the cylinder and boiler during the admission of steam. On the other hand we will suppose the expansion to be complete, so that the final temperature T_3 equals the condenser temperature T_0; and we will also take T_0' and T_0'' as equal to T_0.

The process is founded on equation (48), which, calling the work W', is as follows:

$$W' = Q_1 - T_0 \int_0^{Q_1} \frac{dQ}{T} - T_0 N.$$

Here $Q_1 - T_0 \int_0^{Q_1} \frac{dQ}{T}$ represents the maximum work, corresponding to the case when the cyclical process is reversible; and $T_0 N$ represents the loss of work due to the imperfections which arise from the process not being reversible. For this maximum work we have in the case of the steam-engine the expression already given at the end of § 31, viz.

$$m_1\rho_1 + MC\,(T_1 - T_0) - T_0\left(\frac{m_1\rho_1}{T_1} + MC \log \frac{T_1}{T_0}\right).$$

It only remains to determine N, the uncompensated transformation which occurs in the cyclical process. This transformation arises when the steam is passing into the waste space and into the cylinder, and the data for its determination are already given in § 10. There, by assuming that the mass of steam admitted was at once forced back again into the boiler, and also that everything was brought back by a reversible path to its initial condition, we arrived at a special cyclical process, for which we determined all the quantities of heat imparted to the variable mass, and to which we can now apply the equation

$$N = -\int \frac{dQ}{T}.$$

These quantities of heat, some positive some negative, are as follows:

$$m_1\rho_1,\ -m_2\rho_2,\ \mu_0\rho_0,\ MC(T_1 - T_2) \text{ and } -\mu C(T_2 - T_0).$$

The three first of these are imparted at the constant temperatures T_1, T_2 and T_0 respectively: and the corresponding parts of the integral are $\frac{m_1\rho_1}{T_1}$, $-\frac{m_2\rho_2}{T_2}$ and $\frac{\mu_0\rho_0}{T_0}$. The two last are imparted at temperatures which vary continuously between T_2 and T_1, and between T_2 and T_0 respectively; and the corresponding parts of the integral are

$$MC \log \frac{T_1}{T_2}, \quad \text{and } -\mu C \log \frac{T_2}{T_0}.$$

If we substitute the sum of these quantities for the integral, the last equation becomes

$$N = -\frac{m_1\rho_1}{T_1} + \frac{m_2\rho_2}{T_2} - MC \log \frac{T_1}{T_2} - \frac{\mu_0\rho_0}{T_0} + \mu C \log \frac{T_2}{T_0} \dots (55).$$

Multiplying this expression for N by T_0, and subtracting the product from the expression given above for the maximum work, we obtain finally for W' the equation

$$W' = m_1\rho_1 - \frac{T_0}{T_2} m_2\rho_2 + MC(T_1 - T_0) - (M + \mu) CT_0 \log \frac{T_2}{T_0} + \mu_0\rho \quad \dots\dots\dots (56).$$

To compare this expression for W' with that given in the first of equations (28), we have only to substitute in the latter the value of $m_3\rho_3$ given in the last of those equations, and then put $T_3 = T_0$. The expression thus obtained agrees exactly with that in equation (56).

In the same way we may also deduct the loss of work due to incomplete expansion. For this purpose we must calculate the uncompensated transformation which arises during the passage of steam from the cylinder to the condenser, and then include this in the expression for N. By this calculation, which we shall not here perform at length, we arrive at the same expression for the work as is given in equation (28).

NOTE ON THE VALUES OF $\frac{dp}{dt}$.

Since the differential coefficient $\frac{dp}{dt}$ occurs frequently in researches upon steam, it is important to know how far the convenient method of determination employed by the author is allowable; and for this purpose a few values are here placed side by side for comparison.

The formula employed by Regnault to calculate the pressures of steam in his tables, for temperatures above 100°, is the following:

$$\text{Log}\, p = a - b\alpha^x - c\beta^x,$$

where Log denotes the common system of logarithms, x denotes the temperature from -20^0 to the value under consideration, so that $x = t + 20$, and the five constants have the following values:

$$a = 6{\cdot}2640348,$$

$$\text{Log}\, b = 0{\cdot}1397743,$$

$$\text{Log}\, c = 0{\cdot}6924351,$$

$$\text{Log}\, \alpha = 9{\cdot}994049292 - 10,$$

$$\text{Log}\, \beta = 9{\cdot}998343862 - 10.$$

From this formula we obtain the following equation for $\frac{dp}{dt}$:

$$\frac{1}{p}\frac{dp}{dt} = A\alpha^t + B\beta^t,$$

where α and β have the same values as before, and A and B have the following values:

$$\text{Log}\, A = 8{\cdot}5197602 - 10,$$

$$\text{Log}\, B = 8{\cdot}6028403 - 10.$$

Suppose that from this equation we calculate the value of $\frac{dp}{dt}$ for the temperature 147°, then we obtain

$$\left(\frac{dp}{dt}\right)_{147} = 90{\cdot}115.$$

Next for the approximate method of determination, we obtain from Regnault's tables the pressures

$$p_{148}=3392{\cdot}98,$$

$$p_{146}=3214{\cdot}74,$$

whence $$\frac{p_{148}-p_{146}}{2}=\frac{180{\cdot}24}{2}=90{\cdot}12.$$

This approximate value agrees so closely with the exact value deduced above, that it may be safely used for it in all investigations upon the steam-engine.

With regard to temperatures between 0^0 and 100^0, the formula used by Regnault to calculate the pressures of steam between these limits is the following:

$$\log p=a+ba^t-c\beta^t.$$

Here the constants, by Moritz's improved tables, have the following values:

$$a=4{\cdot}7393707,$$

$$\text{Log } b=8{\cdot}1319907112-10,$$

$$\text{Log } c=0{\cdot}6117407675,$$

$$\text{Log } a=0{\cdot}006864937152,$$

$$\text{Log } \beta=9{\cdot}996725536856-10.$$

From this formula we can again obtain for $\frac{dp}{dt}$ an equation of the form

$$\frac{1}{p}\frac{dp}{dt}=Aa^t+B\beta^t,$$

where the values of a and β are the same as given above, and those of A and B are as follows:

$$\text{Log } A=6{\cdot}6930586-10,$$

$$\text{Log } B=8{\cdot}8513123-10.$$

If we calculate from this equation the value of $\frac{dp}{dt}$ corresponding to a temperature of 70^0, we obtain

$$\left(\frac{dp}{dt}\right)_{70}=10{\cdot}1112.$$

By the approximate method of determination we obtain

$$\frac{p_{71}-p_{69}}{2}=\frac{243{\cdot}380-223{\cdot}154}{2}=10{\cdot}113.$$

This result again agrees sufficiently closely with that obtained from the more exact equation.

TABLE *giving the values for steam of the pressure* p, *its differential coefficient* $\frac{dp}{dt} = g$, *and the product* Tg, *for different temperatures: all expressed in millimetres of mercury.*

t in degrees centi-grade.	*p*	Diff.	*g*	Diff.	*Tg*	Diff.
0°	4·600	0·340	0·329	0·022	90	6
1	4·940	0·362	0·351	0·022	96	7
2	5·302	0·385	0·373	0·024	103	7
3	5·687	0·410	0·397	0·026	110	7
4	6·097	0·437	0·423	0·027	117	8
5	6·534	0·464	0·450	0·029	125	9
6	6·998	0·494	0·479	0·030	134	9
7	7·492	0·525	0·509	0·032	143	9
8	8·017	0·557	0·541	0·033	152	10
9	8·574	0·591	0·574	0·035	162	10
10	9·165	0·627	0·609	0·037	172	11
11	9·792	0·665	0·646	0·039	183	12
12	10·457	0·705	0·685	0·040	195	12
13	11·162	0·746	0·725	0·043	207	13
14	11·908	0·791	0·768	0·046	220	14
15	12·699	0·837	0·814	0·047	234	15
16	13·536	0·885	0·861	0·049	249	15
17	14·421	0·936	0·910	0·052	264	16
18	15·357	0·989	0·962	0·055	280	17
19	16·346	1·045	1·017	0·057	297	18
20	17·391	1·104	1·074	0·060	315	18
21	18·495	1·164	1·134	0·062	333	20
22	19·659	1·229	1·196	0·066	353	21
23	20·888	1·296	1·262	0·069	374	21
24	22·184	1·366	1·331	0·071	395	23
25	23·550	1·438	1·402	0·075	418	24
26	24·988	1·517	1·477	0·079	442	25
27	26·505	1·596	1·556	0·082	467	26
28	28·101	1·681	1·638	0·085	493	27
29	29·782	1·766	1·723	0·089	520	29
30	31·548	1·858	1·812	0·093	549	30
31	33·406	1·953	1·905	0·097	579	32
32	35·359	2·052	2·002	0·101	611	33
33	37·411		2·103		644	

t in degrees centi-grade.	*p*	Diff.	*g*	Diff.	*Tg*	Diff.
33	37·411	2·154	2·103	0·105	644	34
34	39·565	2·262	2·208	0·110	678	36
35	41·827	2·374	2·318	0·114	714	37
36	44·201	2·490	2·432	0·118	751	40
37	46·691	2·611	2·550	0·124	791	41
38	49·302	2·737	2·674	0·128	832	42
39	52·039	2·867	2·802	0·133	874	45
40	54·906	3·003	2·935	0·139	919	46
41	57·909	3·145	3·074	0·144	965	49
42	61·054	3·291	3·218	0·149	1014	50
43	64·345	3·444	3·367	0·155	1064	52
44	67·789	3·601	3·522	0·161	1116	55
45	71·390	3·766	3·683	0·167	1171	57
46	75·156	3·935	3·850	0·173	1228	59
47	79·091	4·112	4·023	0·180	1287	62
48	83·203	4·294	4·203	0·185	1349	64
49	87·497	4·483	4·388	0·193	1413	67
50	91·980	4·679	4·581	0·199	1480	69
51	96·659	4·882	4·780	0·207	1549	72
52	101·541	5·092	4·987	0·213	1621	74
53	106·633	5·309	5·200	0·221	1695	78
54	111·942	5·533	5·421	0·228	1773	80
55	117·475	5·766	5·649	0·237	1853	83
56	123·241	6·006	5·886	0·244	1936	87
57	129·247	6·254	6·130	0·252	2023	89
58	135·501	6·510	6·382	0·260	2112	93
59	142·011	6·775	6·642	0·269	2205	96
60	148·786	7·048	6·911	0·278	2301	100
61	155·834	7·330	7·189	0·286	2401	103
62	163·164	7·621	7·475	0·296	2504	107
63	170·785	7·922	7·771	0·305	2611	111
64	178·707	8·231	8·076	0·314	2722	114
65	186·938	8·550	8·390	0·325	2836	118
66	195·488	8·880	8·715	0·334	2954	123
67	204·368	9·218	9·049	0·344	3077	126
68	213·586	9·568	9·393	0·355	3203	131
69	223·154	9·928	9·748	0·365	3334	135
70	233·082	10·298	10·113	0·376	3469	139
71	243·380	10·680	10·489	0·387	3608	144
72	254·060	11·072	10·876	0·398	3752	149
73	265·132	11·476	11·274	0·410	3901	153
74	276·608	11·892	11·684	0·422	4054	159
75	288·500		12·106		4213	

t in degrees centigrade.	*p*	Diff.	*g*	Diff.	*Tg*	Diff.
75	288·500		12·106		4213	
		12·320		0·433		163
76	300·820		12·539		4376	
		12·759		0·445		168
77	313·579		12·984		4544	
		13·210		0·458		174
78	326·789		13·442		4718	
		13·675		0·471		179
79	340·464		13·913		4897	
		14·152		0·484		185
80	354·616		14·397		5082	
		14·642		0·497		190
81	369·258		14·894		5272	
		15·146		0·511		197
82	384·404		15·405		5469	
		15·664		0·524		202
83	400·068		15·929		5671	
		16·194		0·538		208
84	416·262		16·467		5879	
		16·740		0·552		214
85	433·002		17·019		6093	
		17·299		0·577		220
86	450·301		17·586		6313	
		17·874		0·582		227
87	468·175		18·168		6540	
		18·463		0·597		234
88	486·638		18·765		6774	
		19·067		0·612		240
89	505·705		19·377		7014	
		19·687		0·628		248
90	525·392		20·005		7262	
		20·323		0·644		254
91	545·715		20·649		7516	
		20·975		0·660		262
92	566·690		21·309		7778	
		21·643		0·676		269
93	588·333		21·985		8047	
		22·328		0·694		276
94	610·661		22·679		8323	
		23·031		0·712		285
95	633·692		23·391		8608	
		23·751		0·728		292
96	657·443		24·119		8900	
		24·488		0·747		300
97	681·931		24·865		9200	
		25·213		0·765		309
98	707·174		25·630		9509	
		26·017		0·783		317
99	733·191		26·413		9826	
		26·809		0·787		320
100	760·00		27·200		10146	
		27·59		0·805		328
101	787·59		28·005		10474	
		28·42		0·840		343
102	816·01		28·845		10817	
		29·27		0·855		350
103	845·28		29·700		11167	
		30·13		0·865		356
104	875·41		30·565		11523	
		31·00		0·885		367
105	906·41		31·450		11888	
		31·90		0·915		378
106	938·31		32·365		12266	
		32·83		0·935		388
107	971·14		33·300		12654	
		33·77		0·955		397
108	1004·91		34·255		13051	
		34·74		0·975		407
109	1039·65		35·230		13458	
		35·72		0·990		414
110	1075·37		36·220		13872	
		36·72		1·010		424
111	1112·09		37·230		14296	
		37·74		1·030		434
112	1149·83		38·260		14730	
		38·78		1·060		448
113	1188·61		39·320		15178	
		39·86		1·080		457
114	1228·47		40·400		15635	
		40·94		1·100		467
115	1269·41		41·500		16102	
		42·06		1·125		479
116	1311·47		42·625		16581	
		43·19		1·150		491
117	1354·66		43·775		17072	

t in degrees centigrade.	*p*	Diff.	*g*	Diff.	*Tg*	Diff.
117	1354·66		43·775		17072	
118	1399·02	44·36	44·945	1·170	17574	502
119	1444·55	45·53	46·130	1·185	18083	509
120	1491·28	46·73	47·350	1·220	18609	526
121	1539·25	47·97	48·595	1·245	19146	537
122	1588·47	49·22	49·855	1·260	19693	547
123	1638·96	50·49	51·145	1·290	20253	560
124	1690·76	51·80	52·460	1·315	20827	574
125	1743·88	53·12	53·795	1·335	21410	583
126	1798·35	54·47	55·160	1·365	22009	599
127	1854·20	55·85	56·560	1·400	22624	615
128	1911·47	57·27	57·975	1·415	23248	624
129	1970·15	58·68	59·405	1·430	23881	633
130	2030·28	60·13	60·875	1·470	24533	652
131	2091·90	61·62	62·375	1·500	25199	666
132	2155·03	63·13	63·895	1·520	25877	678
133	2219·69	64·66	65·445	1·550	26571	694
134	2285·92	66·23	67·020	1·575	27277	706
135	2353·73	67·81	68·620	1·600	27997	720
136	2423·16	69·43	70·250	1·630	28732	735
137	2494·23	71·07	71·920	1·670	29487	755
138	2567·00	72·77	73·605	1·685	30252	765
139	2641·44	74·44	75·315	1·710	31030	778
140	2717·63	76·19	77·065	1·750	31828	798
141	2795·57	77·94	78·835	1·770	32638	810
142	2875·30	79·73	80·645	1·810	33468	830
143	2956·86	81·56	82·480	1·835	34312	844
144	3040·26	83·40	84·345	1·865	35172	860
145	3125·55	85·29	86·240	1·895	36048	876
146	3212·74	87·19	88·160	1·920	36939	891
147	3301·87	89·13	90·120	1·960	37850	911
148	3392·98	91·11	92·110	1·990	38778	928
149	3486·09	93·11	94·125	2·015	39721	943
150	3581·23	95·14	96·170	2·045	40680	959
151	3678·43	97·20	98·255	2·085	41660	980
152	3777·74	99·31	100·375	2·120	42659	999
153	3879·18	101·44	102·515	2·140	43671	1012
154	3982·77	103·59	104·690	2·175	44703	1032
155	4088·56	105·79	106·910	2·220	45757	1054
156	4196·59	108·03	109·160	2·250	46830	1073
157	4306·88	110·29	111·430	2·270	47915	1085
158	4419·45	112·57	113·740	2·310	49022	1107
159	4534·36	114·91	116·085	2·345	50149	1127

t in degrees centigrade.	*p*	Diff.	*g*	Diff.	*Tg*	Diff.
159	4534·36	117·26	116·085	2·375	50149	1144
160	4651·62	119·66	118·460	2·410	51293	1165
161	4771·28	122·08	120·870	2·445	52458	1184
162	4893·36	124·55	123·315	2·490	53642	1209
163	5017·91	127·06	125·805	2·510	54851	1222
164	5144·97	129·57	128·315	2·545	56073	1244
165	5274·54	132·15	130·860	2·585	57317	1265
166	5406·69	134·74	133·445	2·620	58582	1286
167	5541·43	137·39	136·065	2·670	59868	1314
168	5678·82	140·08	138·735	2·685	61182	1326
169	5818·90	142·76	141·420	2·725	62508	1348
170	5961·66	145·53	144·145	2·765	63856	1372
171	6107·19	148·29	146·910	2·795	65228	1390
172	6255·48	151·12	149·705	2·830	66618	1412
173	6406·60	153·95	152·535	2·880	68030	1440
174	6560·55	156·88	155·415	2·920	69470	1464
175	6717·43	159·79	158·335	2·935	70934	1476
176	6877·22	162·75	161·270	2·980	72410	1502
177	7039·97	165·75	164·250	3·025	73912	1529
178	7205·72	168·80	167·275	3·060	75441	1550
179	7374·52	171·87	170·335	3·090	76991	1570
180	7546·39	174·98	173·425	3·140	78561	1599
181	7721·37	178·15	176·565	3·170	80160	1619
182	7899·52	181·32	179·735	3·205	81779	1642
183	8080·84	184·56	182·940	3·255	83421	1670
184	8265·40	187·83	186·195	3·280	85091	1688
185	8453·23	191·12	189·425	3·320	86779	1714
186	8644·35	194·47	192·795	3·370	88493	1743
187	8838·82	197·86	196·165	3·400	90236	1763
188	9036·68	201·27	199·565	3·445	91999	1792
189	9237·95	204·75	203·010	3·480	93791	1814
190	9442·70	208·23	206·490	3·515	95605	1837
191	9650·93	211·78	210·005	3·550	97442	1861
192	9862·71	215·33	213·555	3·595	99303	1889
193	10078·04	218·97	217·150	3·645	101192	1919
194	10297·01	222·62	220·795	3·675	103111	1941
195	10519·63	226·32	224·470	3·715	105052	1966
196	10745·95	230·05	228·185	3·750	107018	1991
197	10976·00	233·82	231·935	3·795	109009	2020
198	11209·82	237·64	235·730	3·840	111029	2048
199	11447·46	241·50	239·570	3·885	113077	2077
200	11688·96		243·455		115154	

CHAPTER XII.

ON THE CONCENTRATION OF RAYS OF LIGHT AND HEAT AND ON THE LIMITS OF ITS ACTION.

§ 1. *Object of the Investigation.*

The principle assumed by the author as the ground of the second main principle, viz. that heat cannot of itself, or without compensation, pass from a colder to a hotter body, corresponds to everyday experience in certain very simple cases of the exchange of heat. To this class belongs the conduction of heat, which always takes place in such a way that heat passes from hotter bodies or parts of bodies to colder bodies or parts of bodies. Again as regards the ordinary radiation of heat, it is of course well known that not only do hot bodies radiate to cold, but also cold bodies conversely to hot; nevertheless the general result of this simultaneous double exchange of heat always consists, as is established by experience, in an increase of the heat in the colder body at the expense of the hotter.

Special circumstances may however occur during radiation, which cause the rays, instead of continuing in the same straight line, to change their direction; and this change of direction may be such, that all the rays from a complete pencil of finite section meet together in one point, and there combine their action. This can be accomplished, as is well known, by the use of a burning-mirror or burning-glass; and several mirrors or glasses may even be so arranged, that several pencils of rays from different sources of heat meet together in one point.

For cases of this kind there is no experimental proof that it is impossible for a higher temperature to exist at the point of concentration than is possessed by the bodies from which the rays emanate. Rankine* accordingly, on a special occasion, of which we shall speak in another place, has drawn a particular conclusion, which rests entirely on the assumption that rays of heat can be concentrated by reflection in such a way, that at the focus thus produced a body may be raised to a higher temperature than is possessed by the bodies which emit the rays. If this assumption be correct, the principle enunciated above must be false, and the proof, deduced by means of that principle, of the second fundamental principle of the Mechanical Theory of Heat would thus be overthrown.

As the author was anxious to secure the principle against any doubt of this kind, and as the concentration of rays of heat, with which is immediately connected that of rays of light, is a subject which, apart from this special question, is of much interest from many points of view, he has attempted a closer mathematical investigation of the laws which govern the concentration of rays, and of the influence which this concentration can have on the exchange of heat between bodies. The results are contained in the following sections.

I. REASONS WHY THE ORDINARY METHOD OF DETERMINING THE MUTUAL RADIATION OF TWO SURFACES DOES NOT EXTEND TO THE PRESENT CASE.

§ 2. *Limitation of the treatment to perfectly black bodies, and to homogeneous and unpolarized rays of heat.*

When two bodies are placed in a medium permeable to heat rays, they communicate heat to each other by radiation. Of the rays which fall on one of these bodies, part is in general absorbed, part reflected, part transmitted; and it is known that the power of absorption stands in a simple relation to the power of emission. As it is not here our object to investigate the differences between these relations and the laws to which they conform, we will take one simple case, viz. that in which the bodies are such that they completely absorb all the rays which fall upon them, either actually on the surface, or in a layer so thin that its thickness may be neglected. Such bodies have been named by Kirchhoff, in his well-known and excellent paper on the relation between emission and absorption, "perfectly black bodies*."

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* On the Re-concentration of the Mechanical Energy of the Universe, *Phil. Mag.*, Series IV., Vol. IV. p. 358.

Bodies of this kind have also the maximum power of emission. It was formerly assumed to be beyond question that their intensity of emission depended only on their temperature; so that all perfectly black bodies, at the same temperature and with the same extent of surface, would radiate exactly the same quantity of heat. But as the rays emitted by the body are not homogeneous, but differ according to the scale of colours, the question of emission must be studied with special reference to this scale; and Kirchhoff has extended the foregoing principle, by laying down that perfectly black bodies at equal temperatures send out not only the same total quantity of heat, but also the same quantity of each class of ray. As the distinctions between the rays according to colour have no place in our investigation, we will assume throughout that we have to do with only one known class of ray, or, to speak more accurately, with rays whose wave-length only varies within indefinitely small limits. Whatever is true of this class of rays must similarly be true of any other class; and thus the results obtained from homogeneous heat may easily be extended to heat which contains a mixture of different classes of rays.

With the same object of avoiding unnecessary complications, we will abstain from discussing polarization, and assume that we have only to do with unpolarized rays. The mode of taking polarization into account in such cases has already been explained by Helmholtz and Kirchhoff.

§ 3. *Kirchhoff's formula for the mutual Radiation of two Elements of Surface.*

Let s_1 and s_2 be the surfaces of two perfectly black bodies of the same given temperature; and let us consider two elements of these surfaces ds_1 and ds_2, in order to determine and to compare the quantities of heat which they mutually send to each other by radiation. If the medium, which surrounds the bodies and fills the intervening space, is homogeneous, so that the rays simply pass in straight lines from one surface to the other, it is easy to see that the quantity of heat which ds_1 sends to ds_2 must be the same as that which ds_2 sends to ds_1; if on the contrary this medium is not homogeneous, but there are variations in it which cause the rays to be broken up and reflected, the process is less simple, and a closer investigation is needed to prove whether the same perfect reciprocity holds in this case also. This investigation has been performed in a very elegant manner by Kirchhoff; and his results will be briefly stated here, so far as they relate to the case in which the rays on their way from one element to the other suffer no diminution of strength; in other words in which the breakings up and reflections of the ray take place without loss of power, and there is no absorption during its passage. A few variations will alone be made in the denotation and in the system of coordinates, to produce a better accordance with what follows.

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* Pogg. *Ann.*, Vol. CIX. p. 275.

If two points are given, only one of the infinitely large number of rays sent out by one point can in general attain the other*; or if the rays are so broken up and reflected, that several of them meet in the other point, yet they form in general only a limited number of separate rays, each of which can be treated by itself. The path of such a ray from one point to the other is determined by the condition that the time expended in traversing this path is a minimum, compared with the times which would be expended in traversing all other neighbouring paths between the same points. This minimum time is determined, if where several separate rays meet we investigate only one at a time, by the position of the two points between which it passes; and we will denote it, as Kirchhoff has done, by T.

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* The form of expression that a point sends out an infinitely large number of rays is perhaps, in the strict mathematical sense, inaccurate, since heat and light can only be sent forth from a surface, and not from a mathematical point. It would be more accurate to refer the sending out of the heat or light not to the point itself, but to the element of area at the point. As, however, the conception of a ray is itself only a mathematical abstraction, we may, without fear of misconception, retain the statement that an infinitely large number of rays proceed from each point of the surface. If it were our object to determine quantitatively the heat or light radiated by a surface, it is evident that the size of the surface must be taken into account, and that its elements must be considered, not as points, but as indefinitely small surfaces; the area of which must appear as a factor in the formula expressing the quantity of heat or light radiated from an element of surface.

Returning now to the elements of surface ds_1 and ds_2, we will suppose a plane tangential to the surface to be drawn through one point of each element; and we will treat ds_1 and ds_2 as elements of these planes. In each of these planes let us take any system of rectangular co-ordinates, which we will call x_1, y_1 in the one case, and x_2, y_2 in the other*. If we now take a point on each plane, the time T_1, expended by the ray in passing from one point to the other, is determined, as stated above, by the position of the two points; and this time may therefore be treated as a function of the four co-ordinates of the two points.

On these assumptions Kirchhoff's expression for the quantity of heat, which the element ds_1 sends to the element ds_2 per unit of time, is as follows †:

$$\frac{e_1}{\pi}\left(\frac{d^2T}{dx_1dx_2}\times\frac{d^2T}{dy_1dy_2}-\frac{d^2T}{dx_1dy_2}\times\frac{d^2T}{dy_1dx_2}\right)ds_1ds_2,$$

where π is the well-known ratio between the circumference and diameter of a circle, and e_1 is the intensity of emission of the surface s_1, in the locality of the element ds_1, so that $e_1\,ds_1$ represents the whole quantity of heat radiated by ds_1 per unit of time.

Conversely to express the quantity of heat which ds_2 sends to ds_1, we need only substitute for e_1 in the above expression the quantity e_2, which is the intensity of emission of the surface s_2. Everything else remains unaltered, as being symmetrical with regard to the two elements; for the time T, which a ray expends in traversing the path between two points of the two elements, is the same in whichever direction it is moving. If we now assume that the surfaces, which are supposed to be at the same temperature, radiate equal quantities of heat in the same time, then $e_1 = e_2$; and therefore the quantity of heat sent by ds_1 to ds_2 is exactly the same as that sent by ds_2 to ds_1.

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* Kirchhoff has chosen two planes at right angles to the directions of the rays in the neighbourhood of the two elements; he has taken axes of co-ordinates in these planes, and has projected the elements of surface upon them.

† Pogg. *Ann.*, Vol. CIX. p. 286.

§ 4. *Indeterminateness of the Formula in the case of the Concentration of Rays.*

We have already observed that in general only one ray, or a limited number of separate rays, can pass between two given points. In special cases, however, it may happen, that an indefinitely large number of rays, forming a pencil in either two or three dimensions (i.e. in the latter case forming a cone), and starting from the first point, may again unite in the second. This of course holds with rays of light as well as of heat, and it is usual in Optics to call such a point, in which all the rays of a certain conical pencil sent out from a given point unite again, the image of the given point; or, since conversely the first point may become the image of the second, the two points are called conjugate foci. When what is here described in the case of two particular points holds of all the points of two surfaces, so that every point of the one surface is the conjugate focus of some point on the other surface, then the one surface is called the optical image of the other.

We may now ask how the exchange of rays takes place between the elements of two such surfaces; whether the above-mentioned reciprocity holds, so that at equal temperatures any element of the one surface sends to any element of the other exactly the same amount of heat as it received from it, and therefore one body cannot heat the other to a higher temperature than its own; or whether in such cases the concentration of the rays makes it possible for one body to heat another to a higher temperature than it possesses itself.

To this case Kirchhoff's expression does not directly apply. For let the surface s_2 be an optical image of the surface s_1. Then all the rays, which a point p_1, lying upon s_1, sends out within a certain cone, unite on some point p_2 of the surface s_2, and all the surrounding points of s_2 receive no rays whatever from p_1. Hence if the co-ordinates x_1, y_1 of the point p_1 are given, then the co-ordinates x_2, y_2 of the point p_2 are no longer to be taken at pleasure, but are also fixed; and similarly, if x_2, y_2 are given, then x_1, y_1 are also determined. A differential coefficient of the form $\frac{d^2 T}{dx_1 dx_2}$, where x_1 is considered as variable when differentiating according to x_1, whilst the second co-ordinate y_1 of the same point, and the co-ordinates x_2, y_2 of the other, are assumed to be constant,—and where similarly in differentiating according to x_2, this is taken as the only variable—can thus represent no real quantity of finite value. Therefore in this case we must find an expression of somewhat different form from Kirchhoff's; and for this purpose we must first consider some questions similar to those considered by Kirchhoff in arriving at his expression.

II. DETERMINATION OF CORRESPONDING POINTS AND CORRESPONDING ELEMENTS OF SURFACE IN THREE PLANES CUT BY THE RAYS.

§ 5. *Equations between the co-ordinates of the points in which a ray cuts three given planes.*

Let there be three given planes *a, b, c* (Fig. 25), and in each of them let there be a system of rectangular co-ordinates, which we may call respectively x_ay_a, x_by_b, and x_cy_c. Let us take a point p_a in plane *a*, and a point p_b in plane *b*, and consider a ray as passing from one of these to the other; then to determine its path we have the condition that the time, which the ray expends in traversing it, must be less than it would expend in traversing any other neighbouring path. Call this minimum time T_{ab}. It is a function of the co-ordinates of p_a and p_b, i.e. of the four quantities x_ay_a, x_by_b. Similarly let T_{ac} be the time of the ray's passage between two points p_a and p_c, in planes *a* and *c*; and let T_{bc} be the time of its passage between two points p_b and p_c, in planes *b* and *c*. T_{ac} is a function of the co-ordinates x_ay_a, x_cy_c; and T_{bc} is a function of the co-ordinates x_by_b, x_cy_c.

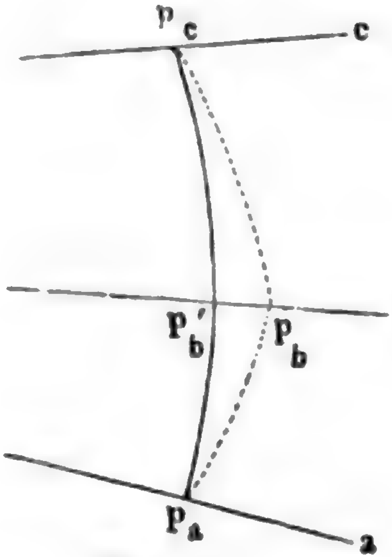

Fig. 25.

Now as a ray, which passes between two of these planes, will in general cut the third plane also, we have for each ray three points of section, which are so related to each other that any one of them is in general determined by the other two. The equations which serve for this determination may be easily deduced from the above-mentioned condition. Let us first suppose that points p_a and p_c are given beforehand, and that the point is still unknown in which the ray cuts the intermediate plane b. This point, to distinguish it from other points in the plane, we will call p'_b. Take any point whatever p_b in this plane, and consider two rays, which we may call auxiliary rays, passing the one from p_a to p_b, and the other from p_b to p_c. In Fig. 25 these rays are shewn by dotted lines, and the primary ray, which goes direct from p_a to p_c, by a full line*. If, as before, we call the times expended by these two rays T_{ab} and T_{bc}, the value of the sum of these times $T_{ab} + T_{bc}$ will depend on the position of p_b, and therefore, since the points p_a and p_c are assumed to be given, it may be considered as a function of the co-ordinates $x_b y_b$ of point p_b. Among all the values, which this sum may assume if we give to point p_b various positions in the neighbourhood of p'_b, the minimum value must be that which is obtained by making p_b coincide with p'_b, in which case the auxiliary rays merely become parts of the direct ray. We therefore have the following two equations to determine the co-ordinates of this point p'_b:

$$\frac{d(T_{ab} + T_{bc})}{dx_b} = 0; \qquad \frac{d(T_{ab} + T_{bc})}{dy_b} = 0 \ldots\ldots\ldots\ldots(1).$$

As T_{ab} and T_{bc}, in addition to the co-ordinates of the unknown point p_b, contain also the co-ordinates of the known points p_a and p_c, we may consider the two equations thus established as being simply two equations between the six co-ordinates of the three points in question. These equations, therefore, can be applied, not merely to determine the co-ordinates of the point in the intermediate plane from those of the two other points, but generally to determine any two of the six co-ordinates from the other four.

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* These lines are shewn curved in the figure, to indicate that the path taken by a ray between two given points need not be simply the straight line drawn between the two points, but a different line determined by the refractions or reflections which the ray may undergo: it may thus be either a broken line, made up of several straight lines, or (if the medium through which it passes changes its character continuously instead of suddenly) a continuous curve.

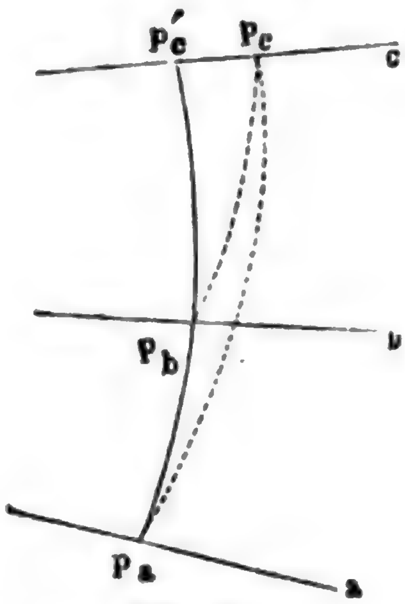

Fig. 26.

Next let us assume that the points p_a and p_b (Fig. 26), in which the ray cuts planes a and b, are given, and that the point is yet unknown in which it cuts plane c. This point let us call p'_c, to distinguish it from other points in the same plane. Take any point p_c in plane c, and consider two auxiliary rays, one of which goes from p_a to p_c, and the other from p_b to p_c. In Fig. 26 these are again shewn dotted, while the primary ray is shewn full. Let T_{ac} and T_{bc} be the times of passage of these auxiliary rays. Then the value of the difference $T_{ac} - T_{bc}$ depends on the position of p_c in plane c. Among the various values obtained by giving to p_c various positions in the neighbourhood of p'_c, the maximum must be that obtained by making p_c coincide with p'_c. For in that case the ray passing from p_a to p_c cuts the plane b in the given point p_b, and is therefore made up of the ray which passes from p_a to p_b and of that which passes from p_b to p_c. Accordingly we may put

$$T_{ac} = T_{ab} + T_{bc}.$$

Hence the required difference is given in this special case by

$$T_{ac} - T_{bc} = T_{ab}.$$

If on the other hand p_c does not coincide with p'_c, then the ray which passes from p_a to p_c does not coincide with the two which pass from p_a to p_b and from p_b to p_c; and since the direct ray between p_a and p_c travels in the shortest time, we must have

$$T_{ac} < T_{ab} + T_{bc},$$

and therefore we have in general for the required difference the inequality

$$T_{ac} - T_{bc} < T_{ab}.$$

This difference is thus generally smaller than in the special case where p_c lies in the continuation of the ray which passes from p_a to p_b, and this special value of the difference thus forms a maximum*. Hence we have the two following conditions:

$$\frac{d(T_{ac}-T_{bc})}{dx_c}=0; \quad \frac{d(T_{ac}-T_{bc})}{dy_c}=0 \text{ ....} (2).$$

If we lastly assume that the points p_b and p_c in the planes b and c are given beforehand, while the point in which the ray cuts the plane a is still unknown, we obtain by an exactly similar procedure the two following conditions:

$$\frac{d(T_{ac}-T_{ab})}{dx_a}=0; \quad \frac{d(T_{ac}-T_{ab})}{dy_a}=0 \text{........} (3).$$

In this way we arrive at three pairs of equations, each of which serves to express the corresponding relation between the three points in which a ray cuts the three planes a, b, c; so that if two of the points are given the third can be found, or, more generally, if of the six co-ordinates of the three points four are given the other two may be determined.

§ 6. *Relation between Corresponding Elements of Surface.*

We will now take the following case. Given on one of the planes, say a, a point p_a, and on another, say b, an element of surface ds_b; then if rays pass from p_a to the different points of ds_b, and if we suppose these rays produced till they cut the third plane c, they will all cut that plane in general within another indefinitely small element of surface, which we will call ds_c (Fig. 27). Let us now determine the relation between ds_b and ds_c.

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* In Kirchhoff's paper (p. 285) it is stated of the quantity there considered, which is essentially the same as the difference here treated of, except that it refers to four planes instead of three, that it must be a *minimum*. This may possibly be a printer's error, and in any case an interchange of maximum and minimum in this place would have no further influence, because the principle used in the calculations which follow, viz., that the differential coefficient = 0, holds equally for a maximum or a minimum.

In this case, of the six co-ordinates which relate to each ray (viz. those of the three points in which the ray cuts the three planes) two, viz. x_a and y_a, are given beforehand. If we now take any values we please for x_b and y_b, the co-ordinates x_c and y_c are in general thereby determined. Thus in this case we may consider x_c and y_c as two functions of x_b and y_b. As the form of the element ds_b may be any whatever, let it be a rectangle dx_b, dy_b, and let us find the point in plane c corresponding to every point in the outline of this rectangle. We shall then have on plane c an indefinitely small parallelogram which forms the corresponding element of surface.

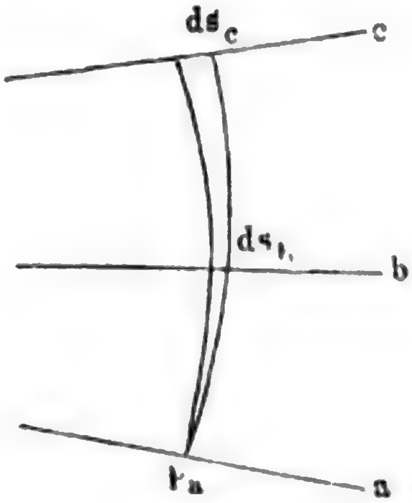

Fig. 27.

The magnitude of this parallelogram is determined as follows. Let λ be the length of the side which corresponds to the side dx_b of the rectangle in plane b, and let (λx_c) and (λy_c) be the angles which this side makes with the axes of co-ordinates. Then

$$\lambda \cos (\lambda x_c) = \frac{dx_c}{dx_b}\, dx_b; \quad \lambda \cos (\lambda y_c) = \frac{dy_c}{dx_b}\, dx_b.$$

Again, let μ be the other side of the parallelogram, and let (μx_c) and (μy_c) be the angles it makes with the axes. Then we have

$$\mu \cos (\mu x_c) = \frac{dx_c}{dy_b}\, dy_b; \quad \mu \cos (\mu y_c) = \frac{dy_c}{dy_b}\, dy_b.$$

Let $(\lambda\mu)$ be the angle between the sides λ and μ. Then we have

$$\cos (\lambda\mu) = \cos (\lambda x_c) \cos (\mu x_c) + \cos (\lambda y_c) \cos (\mu y_c)$$

$$= \left(\frac{dx_c}{dx_b}\frac{dx_c}{dy_b} + \frac{dy_c}{dx_b}\frac{dy_c}{dy_b}\right) \frac{dx_b dy_b}{\lambda\mu}.$$

Now to determine the area ds_c of the parallelogram, we may write

$$ds_c = \lambda\mu \sin(\lambda\mu)$$
$$= \lambda\mu\sqrt{1-\cos^2(\lambda\mu)}$$
$$= \sqrt{\lambda^2\mu^2 - \cos^2(\lambda\mu)\,\lambda^2\mu^2}.$$

Here we may substitute for $\cos(\lambda\mu)$ the expression just given, and for λ^2 and μ^2 the following expressions derived from the above equations:—

$$\lambda^2 = \left\{\left(\frac{dx_c}{dx_b}\right)^2 + \left(\frac{dy_c}{dx_b}\right)^2\right\} dx_b^2,$$
$$\mu^2 = \left\{\left(\frac{dx_c}{dy_b}\right)^2 + \left(\frac{dy_c}{dy_b}\right)^2\right\} dy_b^2.$$

Then several terms under the root cancel each other, and the remainder form a square as follows:

$$ds_c = \sqrt{\left(\frac{dx_c}{dx_b}\frac{dy_c}{dy_b} - \frac{dx_c}{dy_b}\frac{dy_c}{dx_b}\right)^2 dx_b^2\, dy_b^2}$$
$$= \sqrt{\left(\frac{dx_c}{dx_b}\frac{dy_c}{dy_b} - \frac{dx_c}{dy_b}\frac{dy_c}{dx_b}\right)^2 ds_b^2}.$$

This quadratic equation can therefore be solved at once. But it must be observed that the difference within the brackets may be either positive or negative, and, as we have only to do with the positive root, we will denote this by putting the letters v.n. (valor numericus) before this difference. We can then write

$$ds_c = \text{v.n.}\left(\frac{dx_c}{dx_b}\frac{dy_c}{dy_b} - \frac{dx_c}{dy_b}\frac{dy_c}{dx_b}\right) ds_b \ldots\ldots\ldots\ldots(4).$$

To ascertain how x_c and y_c depend upon x_b and y_b, we must apply one of the three pairs of equations in § 5. We will first choose equations (1). If we differentiate those equations according to x_b and y_b, remembering that each of the quantities denoted by T contains two of the three pairs of co-ordinates $x_a, y_a, x_b, y_b, x_c, y_c$, as denoted by the indices; and if in differentiating we treat x_c and y_c as functions of

x_b and y_b, whilst we take x_a and y_a as constant; then we obtain the following four equations:

$$\left.\begin{aligned}
\frac{d^2(T_{ab}+T_{bc})}{(dx_b)^2}+\frac{d^2T_{bc}}{dx_b dx_c}\times\frac{dx_c}{dx_b}+\frac{d^2T_{bc}}{dx_b dy_c}\times\frac{dy_c}{dx_b}=0\\
\frac{d^2(T_{ab}+T_{bc})}{dx_b dy_b}+\frac{d^2T_{bc}}{dy_b dx_c}\times\frac{dx_c}{dy_b}+\frac{d^2T_{bc}}{dx_b dy_c}\times\frac{dy_c}{dy_b}=0\\
\frac{d^2(T_{ab}+T_{bc})}{dx_b dy_b}+\frac{d^2T_{bc}}{dy_b dx_c}\times\frac{dx_c}{dx_b}+\frac{d^2T_{bc}}{dy_b dy_c}\times\frac{dy_c}{dx_b}=0\\
\frac{d^2(T_{ab}+T_{bc})}{(dy_b)^2}+\frac{d^2T_{c}}{dy_b dx_c}\times\frac{dx_c}{dy_b}+\frac{d^2T_{bc}}{dy_b dy_c}\times\frac{dy_c}{dy_b}=0
\end{aligned}\right\}\ldots\ldots(5).$$

If by help of these equations we determine the four differential coefficients $\frac{dx_c}{dx_b}$, $\frac{dx_c}{dy_b}$, $\frac{dy_c}{dx_b}$, $\frac{dy_c}{dy_b}$ and substitute the values thus found in equation (4), we obtain the required relation between ds_b and ds_c. To be able to write the result more briefly, we will use the following symbols:

$$A=\text{v.n.}\left(\frac{d^2T_{bc}}{dx_b dx_c}\times\frac{d^2T_{bc}}{dy_b dy_c}-\frac{d^2T_{bc}}{dx_b dy_c}\times\frac{d^2T_{bc}}{dy_b dx_c}\right)\ldots\ldots(6),$$

$$E=\text{v.n.}\left[\frac{d^2(T_{ab}+T_{bc})}{(dx_b)^2}\times\frac{d^2(T_{ab}+T_{bc})}{(dy_b)^2}-\left\{\frac{d^2(T_{ab}+T_{bc})}{dx_b dy_b}\right\}^2\right]$$
$$\ldots\ldots(7).$$

Then the required relation may be written as follows:

$$\frac{ds_c}{ds_b}=\frac{E}{A}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8).$$

Again, if we suppose in like manner that a point p_c is given on plane c (Fig. 28), and find on plane a the element ds_a, which corresponds to the given element ds_b on plane b, then the result can be derived from that last given by simply interchanging the indices a and c. If for brevity we write

$$C=\text{v.n.}\left(\frac{d^2T_{ab}}{dx_a dx_b}\times\frac{d^2T_{ab}}{dy_a dy_b}-\frac{d^2T_{ab}}{dx_a dy_b}\times\frac{d^2T_{ab}}{dy_a dx_b}\right)\ldots(9),$$

then we have

$$\frac{ds_a}{ds_b}=\frac{E}{C}\text{....................}(10).$$

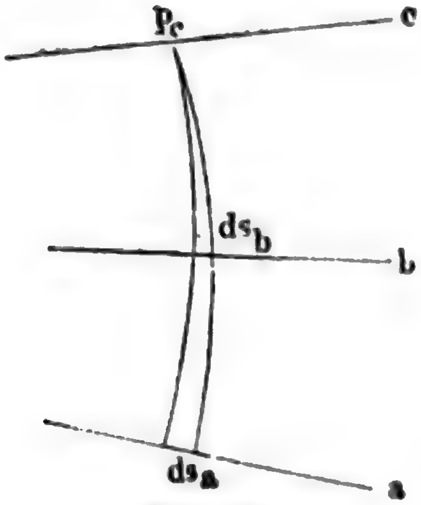

Fig. 28.

Lastly, suppose a point p_b to be given on plane b (Fig. 29)

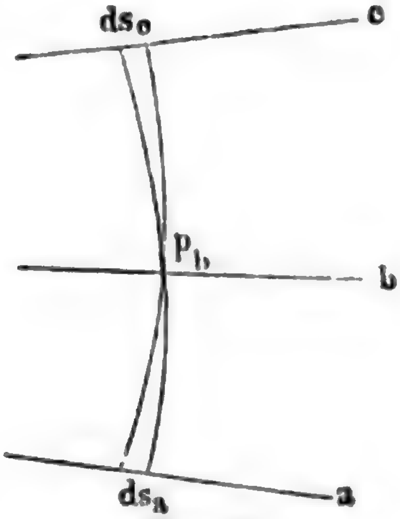

Fig. 29

and choose any element of surface ds_a on plane a. Let us suppose that rays from different points of this element pass through p_b, and that they are produced to the plane c. Then the magnitude of the element of surface ds_c, in which all these rays meet plane c, is found, using the same symbols as before, to be as follows:

$$\frac{ds_c}{ds_a}=\frac{C}{A}\text{.......................}(11).$$

From this we see that the two corresponding elements in this case bear exactly the same relation to each other, as the two elements which are obtained when we have an element ds_b given in plane b, and then, having assumed as the origin of the rays a point first in plane a, and secondly in plane c, determine in each case the element of surface in the third plane corresponding to the element ds_b.

§ 7. *Fractions formed out of six quantities to express the Relations between Corresponding Elements.*

In the last section we have only employed the first of the three pairs of equations in § 5. We can however employ the two other pairs (2) and (3) in the same manner. Each pair leads us to three quantities of the same kind as those already denoted by A, C, and E. These quantities serve to express the relations between the elements of surface. Of the nine quantities thus obtained, however, there are four which are equal to each other, whereby the actual number is reduced to six. The expressions for these six are here placed together for the sake of convenience, although three of them have been already given.

$$\left.\begin{aligned}
A &= \text{v.n.}\left(\frac{d^2T_{bc}}{dx_b dx_c}\times\frac{d^2T_{bc}}{dy_b dy_c}-\frac{d^2T_{bc}}{dx_b dy_c}\times\frac{d^2T_{bc}}{dy_b dx_c}\right)\\
B &= \text{v.n.}\left(\frac{d^2T_{ac}}{dx_a dx_c}\times\frac{d^2T_{ac}}{dy_a dy_c}-\frac{d^2T_{ac}}{dx_a dy_c}\times\frac{d^2T_{ac}}{dy_a dx_c}\right)\\
C &= \text{v.n.}\left(\frac{d^2T_{ab}}{dx_a dx_b}\times\frac{d^2T_{ab}}{dy_a dy_b}-\frac{d^2T_{ab}}{dx_a dy_b}\times\frac{d^2T_{ab}}{dy_a dx_b}\right)\\
D &= \text{v.n.}\left\{\frac{d^2(T_{ac}-T_{ab})}{(dx_a)^2}\times\frac{d^2(T_{ac}-T_{ab})}{(dy_a)^2}-\left[\frac{d^2(T_{ac}-T_{ab})}{dx_a dy_a}\right]^2\right\}\\
E &= \text{v.n.}\left\{\frac{d^2(T_{ab}+T_{bc})}{(dx_a)^2}\times\frac{d^2(T_{ab}+T_{bc})}{(dy_b)^2}-\left[\frac{d^2(T_{ab}+T_{bc})}{dx_b dy_b}\right]^2\right\}\\
F &= \text{v.n.}\left\{\frac{d^2(T_{ac}-T_{bc})}{(dx_c)^2}\times\frac{d^2(T_{ac}-T_{bc})}{(dy_c)^2}-\left[\frac{d^2(T_{ac}-T_{bc})}{dx_c dy_c}\right]^2\right\}
\end{aligned}\right\}$$

$$\ldots\ldots\ldots(\text{I.})$$

By help of these six quantities every relation between two elements of surface can be expressed by three different fractions, as may be shewn in tabular form as follows:

$$\left.\begin{array}{l} \dfrac{ds_c}{ds_b}=\dfrac{E}{A}=\dfrac{A}{F}=\dfrac{C}{B} \\[2ex] \dfrac{ds_b}{ds_a}=\dfrac{C}{E}=\dfrac{B}{A}=\dfrac{D}{C} \\[2ex] \dfrac{ds_a}{ds_c}=\dfrac{A}{C}=\dfrac{F}{B}=\dfrac{B}{D} \end{array}\right\} \dots\dots\dots\dots\dots \text{(II.)}.$$

It is easily seen that the three horizontal rows relate to the three cases, in which the given point through which the rays must pass is taken either in plane *a*, plane *c*, or plane *b*. Of the three vertical rows of fractions, which express the relations between the elements of surface, the first is deduced from equation (1) of § 5, the second from (2) and the third from (3).

Since the three fractions, which express a given relation between two elements of surface, must be equal to each other, we have the following equations between the six quantities:

$$D=\frac{BC}{A};\quad E=\frac{CA}{B};\quad F=\frac{AB}{C} \dots\dots\dots \text{(12)},$$

$$A^2=EF;\quad B^2=FD;\quad C^2=DE \dots\dots\dots \text{(13)}.$$

Our further investigations will be performed by means of these six quantities; and since every relation between two elements of surface is expressed by three different fractions, we can always choose amongst these the fraction most suitable for each special case.

III. DETERMINATION OF THE MUTUAL RADIATION, WHEN THERE IS NO CONCENTRATION OF RAYS.

§ 8. *Magnitude of the Element of Surface corresponding to* ds_c *on a plane in a particular position.*

We will first consider the case to which Kirchhoff's expression refers, and seek to determine how much heat two elements send out to each other, on the assumption that every point of one element receives from every point of the other one ray and only one; or at most a limited number of particular rays, which may be considered separately.

Given two elements ds_a and ds_c in planes a and c (Fig. 30), we will first determine the heat which ds_a sends to ds_c. For this purpose let us suppose the intermediate plane b to lie parallel to plane a at a distance ρ, which is so small, that the part which lies between these two planes of any ray passing from ds_a to ds_c may be considered as a straight line, and the medium through which it passes as homogeneous. Let us now take any point in element ds_a, and consider the pencil of rays which passes from this point to the element ds_c. This pencil will cut plane b in an element ds_b whose magnitude is given by one of the three fractions in the uppermost horizontal row of equations (II.). Choosing the last of these we have the equation

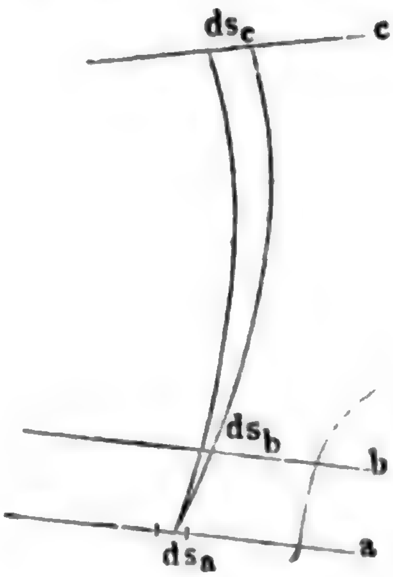

Fig. 30.

$$ds_b = \frac{B}{C} ds_c \ldots\ldots\ldots\ldots\ldots\ldots\ldots (14).$$

The quantity C may in this case be brought into a specially simple form, on account of the special position of plane b. For this purpose let us follow Kirchhoff in choosing the system of co-ordinates in b so as to correspond exactly with that in the parallel plane a; i.e. let the origins of both lie in a common perpendicular to the two planes and let each axis of one system be parallel to the corresponding axis of the other. Let r be the distance between two points lying on the two planes, and having co-ordinates x_a, y_a and x_b, y_b respectively. Then

$$r = \sqrt{\rho^2 + (x_b - x_a)^2 + (y_b - y_a)^2} \ldots\ldots\ldots\ldots (15).$$

Let us now suppose a single ray to pass from one of these points to the other; then, since its motion between the two planes is supposed to be rectilinear, the length of its path will be simply represented by r; and if we denote by v_a its velocity in the neighbourhood of plane a, which by the assumption will remain nearly constant between a and b, then the time which the ray expends in the passage will be given by the equation

$$T_{ab}=\frac{r}{v_a}.$$

The expression for C may therefore be written

$$C=\text{v.n.}\frac{1}{v_a^2}\left(\frac{d^2r}{dx_a dx_b}\times\frac{d^2r}{dy_a dy_b}-\frac{d^2r}{dx_a dy_b}\times\frac{d^2r}{dy_a dx_b}\right).$$

Substituting for r its value as given by (15), we obtain

$$C=\frac{1}{v_a^2}\times\frac{\rho^2}{r^4}\dots\dots\dots\dots\dots\dots\dots (16).$$

Hence equation (14) becomes

$$ds_b=v_a^2\times\frac{r^4}{\rho^2}Bds_c\dots\dots\dots\dots\dots\dots (17).$$

If we denote by θ the angle which the indefinitely small pencil of rays, which starts from a point on ds_a, makes with the normal at that point, then $\cos\theta=\frac{\rho}{r}$; and the last equation also takes the form

$$ds_b=\frac{v_a^2r^2}{\cos^2\theta}Bds_c\dots\dots\dots\dots\dots\dots (18).$$

§ 9. *Expressions for the quantities of Heat which* ds_a *and* ds_c *radiate to each other.*

When the magnitude of the element of surface ds_b is determined, the quantity of heat which ds_a sends to ds_c can be easily expressed.

From every point of ds_a an indefinitely small pencil of rays goes to ds_c; and the solid angle of the cone made by the pencil from each of these points may be taken as the same. The magnitude of this angle is determined by the magnitude and position of that element ds_b in which the cone cuts plane b. To express this angle geometrically, let us suppose that a sphere of radius ρ is drawn round the point from which the rays start, and that within this sphere we may consider the path of the rays as being rectilinear. If $d\sigma$ is the element of surface in which this sphere is cut by the pencil of rays, then $\frac{d\sigma}{\rho^2}$ represents the angle of the cone. But since the element ds_b is at the distance r from the vertex of the cone, and since the normal to the surface at ds_b, which is parallel to the already mentioned normal to the surface at ds_a, forms with the indefinitely small cone of rays the angle θ, we have the equation

$$\frac{d\sigma}{\rho^2} = \frac{\cos\theta \times ds_b}{r^2} \qquad \text{.................. (19).}$$

If we substitute for ds_b its value from (18), we obtain

$$\frac{d\sigma}{\rho^2} = \frac{v_a^2}{\cos\theta} B ds_a \qquad \text{.................. (20).}$$

We have now to determine the magnitude of that part of the heat sent from ds_a which corresponds to this indefinitely small cone; or in other words, how much heat ds_a sends through the given element $d\sigma$ upon the spherical area. This quantity of heat is proportional (1) to the magnitude of the radiating element ds_a, (2) to the angle of the cone, or to $\frac{d\sigma}{r^2}$, and (3), according to the well-known law of radiation, to the cosine of the angle θ, which the indefinitely small cone makes with the normal. It may therefore be expressed by

$$\epsilon \cos\theta \frac{d\sigma}{\rho^2} ds_a,$$

where ϵ is a factor depending on the temperature of the surface. To determine this factor we have the condition that the whole quantity of heat which ds_a radiates, or which it sends to the whole surface of any hemisphere above plane a, must equal $e_a ds_a$ where e_a is the intensity of emission from plane a at the position of ds_a. Hence we have

$$\frac{\epsilon}{\rho^2}\int \cos\theta \, d\sigma = e_a.$$

The integration extends over the whole of the hemisphere, and gives

$$\epsilon\pi = e_a.$$

Substituting this value of e in the above expression, we obtain for the quantity of heat which ds_a sends through $d\sigma$ the formula

$$\frac{e_a}{\pi}\cos\theta\frac{d\sigma}{\rho^2}ds_a.$$

We have only to substitute in this formula the value for $\frac{d\sigma}{\rho^2}$ given in equation (20), and we obtain the required expression for the quantity of heat which ds_a sends to ds_c, viz.:

$$e_a v_a^2\frac{B}{\pi}ds_a ds_c.$$

If conversely we require the quantity of heat which ds_c sends to ds_a, and if we denote by e_c the intensity of emission from plane c at the position of ds_c, and by v_c the velocity of the rays in the neighbourhood of ds_c, we obtain the expression:

$$e_c v_c^2\frac{B}{\pi}ds_a ds_c.$$

§ 10. *Radiation as dependent on the surrounding Medium.*

The expressions obtained in the last section are in general the same as Kirchhoff's expression given in § 3, and differ only inasmuch as they contain as factor the square of the velocity, which does not occur in Kirchhoff's expression, because he considers nothing but the velocity in vacuo, and takes this as unity. Since however the bodies, whose mutual radiation we are considering, may often be in different media, where the velocity of the rays is different, this factor is not without importance; and its introduction leads also to a special conclusion of some theoretical interest.

As mentioned in § 2, it has been hitherto assumed that with perfectly black bodies the intensity of emission depends only on the temperature, so that two such bodies of equal temperature would radiate equal quantities of heat from equal areas of surface. As far as the author knows, the question whether the surrounding medium has also an influence on the intensity of emission has never been considered. Since however the two expressions given above for the mutual radiation of two elements contain a factor which depends on the nature of the medium, it becomes necessary to consider this medium, and the method of determining its influence.

If from the above two expressions we omit the factor which is common to both, viz. $\frac{B}{\pi} ds_a ds_c$, we have the result that the quantity of heat, which the element ds_a sends to the element ds_c, bears to that which ds_c sends to ds_a the ratio $e_a v_a^2 : e_c v_c^2$. If we now assume that at equal temperatures the radiation is always equal, even when the media in contact with the two elements are different, then for equal temperatures we must put $e_a = e_c$; and the quantities of heat, which the two elements radiate to each other, would then not be equal, but would be in the ratio $v_a^2 : v_c^2$. It would follow that two bodies which are in different media, e.g. one in water and the other in air, would not tend to equalize their temperatures by mutual radiation, but that one would be able by radiation to raise the other to a higher temperature than that which itself possesses.

If on the other hand we maintain the universal correctness of the fundamental principle laid down by the author, viz. that heat cannot of itself pass from a colder to a hotter body, then we must consider the mutual radiations of two perfectly black elements of equal temperature as being themselves equal, and must therefore put

$$e_a v_a^2 = e_c v_c^2 \text{ .... } (21).$$

Hence

$$e_a : e_c :: v_c^2 : v_a^2 \text{ .... } (22).$$

Since the ratio of the velocities is the reciprocal of that of the coefficients of refraction, which we may call n_a and n_c, this proportion may be written

$$e_a : e_c :: n_a^2 : n_c^2 \text{ .... } (23).$$

Hence the radiation of perfectly black bodies at equal temperatures is different in different media, and varies inversely as the squares of the velocities in those media, or directly as the squares of the coefficients of refraction. Thus the radiation in water must bear to that in air the ratio $(\frac{4}{3})^2 : 1$, nearly.

We have also to remember that in the heat radiated from perfectly black bodies there are rays of very different wave-lengths; and if we assume that the equality of mutual radiation holds, not merely for the heat as a whole, but also for each wave-length in particular, we must have for each of these a proportion similar to (22) and (23) but in which the quantities in the right-hand ratio have somewhat different values.

Lastly, instead of perfectly black bodies, let us consider bodies in which the absorption of the rays received is partial only. We must then introduce in the formula, in place of the emission, a fraction having the emission as numerator and the coefficient of absorption as denominator. For this fraction we can obtain relations similar to those obtained for the emission alone. This generalization, in which the influence of the direction of the rays upon the emission and absorption must also be taken into account, need not here be entered upon.

IV. DETERMINATION OF THE MUTUAL RADIATION OF TWO ELEMENTS OF SURFACE, IN THE CASE WHEN ONE IS THE OPTICAL IMAGE OF THE OTHER.

§ 11. *Relations between* B, D, F *and* E.

We have hitherto assumed that the planes *a* and *c*, so far as we are concerned with them, give out their rays in such a way, that one ray and one only, or at most a limited quantity of individual rays, pass from any point in the one to any point in the other. We will now pass on to the case in which this does not hold. The rays which diverge from points in the one plane may be made to converge by reflections or refractions, and to meet again on the other plane; so that for any point p_a on plane *a* there may be one or more points or lines on plane *c*, in which an indefinitely large number of the rays coming from p_a cut that plane, whilst other parts of the same plane receive no rays whatever from p_a. The same of course holds of the rays which start from plane *c* and arrive at plane *a*, since the rays passing to and fro between the same points describe the same paths.

Among the innumerable cases of this description we will,

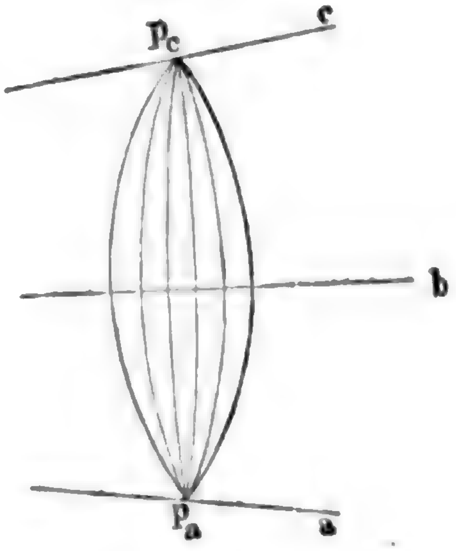

Fig. 31.

for the sake of clearness, consider first the extreme case illustrated in Fig. 31. In this case all the rays sent out by p_a within a certain definite cone meet again in a single point p_c of plane c. This case occurs for example, when the deflection of the rays is effected by a lens, or by a spherical mirror, or by any system of concentric lenses or mirrors. We are here supposed to neglect the spherical and chromatic aberration, which we have a right to do with regard to the latter, inasmuch as we have confined ourselves to homogeneous rays. Two points thus corresponding to each other, as the points of starting and of re-union of the rays, are called, as already mentioned, conjugate foci. For each ray in such a case the co-ordinates x_c, y_c of the point p_c in which it strikes plane c, are determined by the co-ordinates x_a, y_a of the starting point p_a. The other points on plane c in the neighbourhood of p_c receive no rays from p_a; for there is no path to them which has the property that the time in which the ray would traverse it is a minimum, as compared with the time in which it would traverse any other adjacent path. Hence the quantity T_{ac}, which expresses this minimum time, can have a real value only for p_c, and not for any of the points round it. The differential coefficients of T_{ac}, in which the co-ordinates x_a, y_a are assumed to be constant and one of the co-ordinates x_c, y_c to be variable, (or conversely x_c, y_c to be constant and one of the co-ordinates x_a, y_a to be variable) can thus have no real finite values. It follows that of the six quantities A, B, C, D, E, F, which have been determined by equations (I.), the three B, D, F are not applicable to the present case, inasmuch as they contain differential coefficients of T_{ac}; whilst the three others A, C, E contain only differential coefficients of T_{ab} and T_{bc}. Let us now assume that plane b is so chosen that between it and the planes a and c, so far as we are concerned with them, the radiation takes place on the former system, so that one ray and one only, or at most a limited number of rays, pass from any point on plane b to any point on plane a or c. Then for all the points with which we are concerned, the quantities T_{ab} and T_{bc} and their differential coefficients have real values not indefinitely large. The quantities A, C and E are then as applicable in this case as in the former.

One of these quantities, E, takes in this case a special value, which may at once be found. For the three points in which the ray cuts the three planes a, b, c, the two equations given in (1) must hold, viz.:

$$\frac{d(T_{ab}+T_{bc})}{dx_b}=0;\quad \frac{d(T_{ab}+T_{bc})}{dy_b}=0.$$

In the present case the position of the point in which the ray cuts plane b is not determined by the position of the two points p_a and p_c, but plane b may be cut in all points of a certain finite area. Hence the two equations above must hold for all these points, and therefore the equations obtained by differentiating these according to x_b and y_b must also hold, viz.:

$$\frac{d^2(T_{ab}+T_{bc})}{dx_b^2}=0;\ \frac{d^2(T_{ab}+T_{bc})}{dx_b dy_b}=0;\ \frac{d^2(T_{ab}+T_{bc})}{dy_b^2}=0\ \ldots (24).$$

If we apply this to the equation determining E in equations (I.), we obtain

$$E=0.\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (25).$$

The two other quantities A and C have in general finite values, which differ in different circumstances, and which we must now use in our further investigation.

§ 12. *Application of* A *and* C *to determine the Relation between the Elements of Surface.*

Let us suppose that the element ds_a on plane a has an optical image ds_c on plane c, so that every point of ds_a has a point on ds_c as its conjugate focus, and vice versâ. We have now to enquire whether the quantities of heat, which these elements send to each other, when taken as elements of the surfaces of two perfectly black bodies of equal temperatures, are equal or not.

First to determine the position and magnitude of the image ds_c corresponding to the given element ds_a. Take any point p_b on the intermediate plane b, and consider all the rays starting from points on ds_a, which pass through p_b. Each of these rays strikes plane c in the conjugate focus to that from which it starts; and therefore the element of surface in which this pencil of rays cuts plane c is precisely the optical image ds_c of the element ds_a. Therefore, to express the ratio between the areas of ds_c and ds_a, we may use one of the three fractions in the lowest row of equations (II.), which express the relation between the two elements of surface, in which an indefinitely small pencil, passing through a single point p_b of plane b, cuts the two planes a and c. Of these three fractions the first is alone applicable in this case, since the other two are undetermined. We have thus the equation

$$\frac{ds_a}{ds_c} = \frac{A}{C} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (26).$$

This equation is interesting also from an optical point of view, as being the most general equation which can be given to determine the ratio between the area of an object and that of its optical image. It should be remarked that the intermediate plane b, to which the quantities A and C are related, may be any whatever, and can therefore in any particular case be chosen as is most convenient for calculation.

§ 13. *Relation between the Quantities of Heat which* ds_a *and* ds_c *radiate to each other.*

Having thus determined the element of surface ds_c, which forms the image of ds_a, let us take on plane b, instead of a single point, an element of surface ds_b, and let us consider the rays which the two elements ds_a and ds_c send through this element ds_b. All the rays, which start from one point of ds_a and pass through ds_b, unite again in one point of ds_c; and thus all the rays which ds_a sends through ds_b exactly strike the element ds_c, and vice versâ. The two quantities of heat which ds_a and ds_c send to ds_b are thus the same as the quantities of heat which ds_a and ds_c send to each other through the intermediate element ds_b. These quantities of heat are therefore given at once by what has gone before. Thus for the quantity of heat which ds_a sends to ds_b, the same expression will hold, as held in § 9 for the quantity of heat which ds_a sends to ds_c, provided we substitute C for B and ds_b for ds_c. The expression thus becomes

$$e_a v_a^2 \frac{C}{\pi} ds_a \, ds_b.$$

Similarly for the quantity of heat which ds_c sends to ds_b, the expression will be the same as that for the quantity of heat which ds_c sends to ds_a, provided we substitute A for B and ds_b for ds_a, or will be

$$e_c v_c^2 \frac{A}{\pi} ds_c ds_b.$$

Remembering that by equation (26)

$$C ds_a = A ds_c,$$

we see that these two expressions stand to each other in the ratio $e_a v_a^2 : e_c v_c^2$.

We obtain precisely the same result, if we take any other element ds_b on plane b, and consider the quantities of heat which the two elements ds_a and ds_c send to each other through this new element. These will always be found to stand to each other in the ratio $e_a v_a^2 : e_c v_c^2$. Since the quantities of heat, which ds_a and ds_c send to each other on the whole, are made up of those which they send to each other through all the different elements of the intermediate plane, the same ratio must hold for the whole; and we thus obtain the final result, that the total quantities of heat which ds_a and ds_c radiate to each other, stand in the ratio $e_a v_a^2 : e_c v_c^2$.

This is the same relation as was found in sections 8 and 9 for the case where there is no concentration of rays; it thus follows that the concentration of rays, however much it alters the absolute magnitudes of the quantities of heat which two elements radiate to each other, leaves the ratio between them exactly the same.

It was shewn in § 10, that if in the case of ordinary unconcentrated radiation the principle holds that heat cannot pass from a colder to a hotter body, then the radiation must differ in different media, and must be such that for perfectly black bodies of equal temperatures

$$e_a v_a^2 = e_c v_c^2.$$

If this equation is satisfied, then in the present case also, where the elements ds_a and ds_c are images one of the other, the quantities of heat which they mutually radiate must be equal; and therefore, in spite of the concentration of the rays, one element cannot raise the other to a higher temperature than its own.

V. RELATION BETWEEN THE INCREMENT OF AREA AND THE RATIO OF THE TWO SOLID ANGLES OF AN ELEMENTARY PENCIL OF RAYS.

§ 14. *Statement of the Proportions for this Case.*

As an immediate result of the foregoing we may here develope a proportion, which appears to have some general interest, inasmuch as it illustrates a peculiar difference in the behaviour of a pencil of rays in the case of an object and of its image. This difference must always exist and have a determinate value, when the object and the image have different areas.

Consider an indefinitely small pencil of rays, which starts from a point on ds_a, passes through the element ds_b on the intermediate plane, and then unites again in a point on ds_c. We may compare the divergence of the rays at their starting point with the convergence of the same at their point of re-union. This divergence and convergence (or, to use the ordinary phrase, the solid angles of the indefinitely small cones, which the pencil forms at its points of starting and re-union) are given directly by the same method which we have used in § 9, as follows:—

Suppose that round each of the points there is described a sphere of so small a radius, that we may consider the rays as going in straight lines as far as the surface of this sphere; and then consider the element of surface in which the pencil of rays cuts the sphere. Let $d\sigma$ be this element and let ρ be the radius of the sphere; then the angle of the indefinitely small cone, which contains the rays so far as they are rectilinear, will be expressed by $\frac{d\sigma}{\rho^2}$. This fraction we have determined for a similar case in § 9 by equation (20), and in the expression there given we have only to alter the letters in order to transform it into the expression for the present case. In order to express the angle of the cone for that starting point of the rays which lies in plane a, we have only to substitute in that expression ds_b for ds_c, and C for B. In addition, the symbol θ, which expresses the angle between the pencil of rays and the normal to the surface of ds_b, may be changed to θ_a, so as to express more clearly that it relates to plane a; and for the same reason the suffix a may be added to $\frac{d\sigma}{\rho^2}$. Thus we obtain

$$\left(\frac{d\sigma}{\rho^2}\right)_a = \frac{v_a^2}{\cos\theta_a} C ds_b \dots\dots\dots\dots\dots\dots (27).$$

To obtain the other equation, which gives the angle of the cone at the point of re-union on plane c, we have only to change the suffix a into c throughout, and also to substitute A for C. Thus we have

$$\left(\frac{d\sigma}{\rho^2}\right)_c = \frac{v_c^2}{\cos\theta_c} A ds_c \dots\dots\dots\dots\dots\dots (28).$$

From these two equations we obtain the proportion

$$\frac{\cos\theta_a}{v_a^2}\left(\frac{d\sigma}{\rho^2}\right)_a : \frac{\cos\theta}{v_c^2}\left(\frac{d\sigma}{\rho^2}\right)_c :: C : A :: ds_c : ds_a \dots\dots (29),$$

since by equation (26) $Cds_a = Ads_c$.

If we substitute for the velocity the coefficient of refraction, this proportion becomes

$$n_a^2 \cos\theta_a \left(\frac{d\sigma}{\rho^2}\right)_a : n_c^2 \cos\theta_c \left(\frac{d\sigma}{\rho^2}\right)_c :: ds_c : ds_a \dots\dots (30).$$

Here the ratio on the right-hand side is the ratio between the area of an element of surface of the image, and the area of the corresponding element of the object, or in short the proportionate increment of area; and we thus obtain a simple relation between this increment and the ratio of the angles of the cones made by an elementary pencil of rays. It is easily seen that it is not necessary for the truth of this proportion that the rays should finally converge, and meet at one point, but they may also be divergent, in which case their directions meet in one point when produced backwards, and form what is called in optics a virtual image.

If we take the special case in which the medium at the point of starting and of re-union is the same (e.g. where the rays issue from an object which is in air, and, after certain refractions or reflections, form an image which really or virtually is also in air), then $v_a = v_e$ and $n_a = n_e$; whence we have

$$\cos\theta_a \left(\frac{d\sigma}{\rho^2}\right)_a : \cos\theta_e \left(\frac{d\sigma}{\rho^2}\right)_e :: ds_e : ds_a.$$

If we add the further condition, that the pencil of rays makes equal angles with the two elements of surface (e.g. that both are right angles), then we have

$$\left(\frac{d\sigma}{\rho^2}\right)_a : \left(\frac{d\sigma}{\rho^2}\right)_e :: ds_e : ds_a.$$

In this case the angles of the cones formed by the pencil of rays at the object and at the image stand simply in the inverse ratio of the areas of the corresponding elements of object and image.

In the valuable demonstration which Helmholtz has given in his "Physiological Optics"* of the laws of refraction in the case of spherical surfaces, he seeks to connect with these the case of the refractions which take place in the eye; and he finds in page 50, and extends further in page 54, an equation which expresses the relation between the size of the image and the convergence of the rays, for the case in which the change of direction of the rays takes place by refraction or by reflection at the surface of co-axial spheres, and in which the rays are approximately perpendicular to the planes which contain the object and the image. The author however believes that the relation has not before been given in its general form, as in proportions (29) and (30).

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* **Karsten's** ***Universal Encyclopedia of Physics.***

VI. GENERAL DETERMINATION OF THE MUTUAL RADIATION BETWEEN TWO SURFACES, IN THE CASE WHERE ANY CONCENTRATION WHATEVER MAY TAKE PLACE.

§ 15. *General View of the Concentration of Rays.*

We must now extend our investigation so as to embrace not only the extreme case, in which all the rays which issue from a point on plane a within a certain finite cone unite again in one point forming a conjugate focus on plane c, but also every conceivable case of the concentration of rays.

To obtain a closer view of the phenomena of concentration, we may use the following definition. If rays issue from any point p_a and fall on plane c, and if these rays when close to that plane have such directions that on one part of the plane the density of the impinging rays is indefinitely great compared to the mean density, then at this part there is concentration of the rays which issue from p_a. With this definition we may easily treat mathematically the case of concentration. Between point p_a and plane c take any intermediate plane b, which is so placed that there is no concentration in it of the rays issuing from p_a; and also that its relation to plane c is such, so far as we are concerned, that the pencils of rays issuing from points on one of those planes suffer no concentration on the other. Now consider an indefinitely small pencil, which starts from p_a and cuts the planes b and c. Let us compare the areas of the elements ds_b and ds_c in which these planes are cut. If ds_c vanishes in comparison to ds_b, so that we may put

$$\frac{ds_c}{ds_b} = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (31),$$

this is a sign that there is a concentration of rays, in the sense defined above, at plane c.

Let us now return to equations (II.) of § 7. The equations in the first horizontal row are those that refer to the present case: and of the three fractions, which there represent the ratio of the elements of surface, the first applies to our case, because under the assumption made as to the position of the intermediate plane we may determine A and E in the ordinary manner. We have thus the equation

$$\frac{ds_c}{ds_b}=\frac{E}{A}.$$

This fraction can only equal zero if the numerator E is zero, since under the assumption made as to the position of the intermediate planes the denominator A cannot be indefinitely large. We have then as a mathematical criterion, whether the rays issuing from p_a suffer concentration at plane c or not, the condition

$$E=0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(32),$$

which must be fulfilled where there is concentration.

Now assume conversely that on plane c a point p_c is given, and that we have to decide whether the rays issuing from this point suffer concentration at any part of plane a. Then we have in the same way the condition $\frac{ds_a}{ds_b}=0$; and since by (II.) $\frac{ds_a}{ds_b}=\frac{E}{C}$, we arrive at the same final condition

$$E=0.$$

It is in fact easy to see that when the rays issuing from a point on plane a suffer concentration at plane c, then conversely the rays issuing from the latter point must suffer concentration on plane a.

Since equations (13) express the relations which hold between the six quantities A, B, C, D, E, F, we may apply those equations to ascertain what becomes of B, D and F, in the case where $E=0$, whilst A and C have finite values. By those equations

$$B=\frac{AC}{E}; \qquad D=\frac{C^2}{E}; \qquad F=\frac{A^2}{E} \ldots\ldots\ldots\ldots(33).$$

Hence it follows that all three quantities must in the present case be indefinitely great.

§ 16. *Mutual Radiation of an Element of Surface and of a Finite Surface, through an Element of an Intermediate Plane.*

We will now attempt so to determine the ratio between the quantities of heat which two surfaces radiate to each other, that the result must hold in all cases, independently of the question whether there is any concentration of heat or no.

For greater generality we will substitute for the planes a and c, as hitherto considered, two surfaces of any kind, which we may call s_a and s_c. Between them let us take any third surface s_b, which need only fulfil the condition that the rays which pass from s_a to s_c, or vice versâ, suffer no concentration in s_b. Now choose in s_a any element ds_a, and in s_b an element ds_b, so situated that the rays which pass through it from ds_a will when produced strike the surface s_c. Then we will first determine how much heat ds_a sends through ds_b to the surface s_c, and how much heat it receives back from s_c through the same element of the intermediate plane. To ascertain the first mentioned quantity of heat, we have only to determine how much heat ds_a sends to ds_b, since, by our assumption as to the position of ds_b, all this heat after passing ds_b must strike the surface s_c. This quantity of heat may be expressed at once by means of our previous formulae. Suppose a tangent plane to be drawn to s_a at a point of the element ds_a, and similarly a tangent plane s_b at a point of ds_b; and consider the given elements of surface as elements of these planes. If in these tangent planes we take two systems of co-ordinates x_a, y_a, and x_b, y_b, and if we form the quantity C by means of the third of equations (I.), then the required quantity of heat, which ds_a sends through ds_b to the surface s_c, is given by the expressions

$$e_a v_a^2 \frac{C}{\pi} ds_a ds_b.$$

Next with regard to the quantity of heat which ds_a receives through ds_b from the surface s_c, the relations of the points in s_c, from which these rays issue, are not in general so simple as that which holds in the special case, where ds_a has an optical image ds_c lying on s_c, and therefore is also itself the optical image of ds_c. If we choose a known point p_b on the intermediate element ds_b, and consider the rays which pass through this point from all points of ds_a, we have an indefinitely small pencil of rays, cutting s_c in a certain element of surface. It is this element which sends rays to ds_a through the selected point p_b. But if we now choose another point of ds_b as the vertex of the pencil, we arrive at a somewhat different element on the surface s_c. Thus the rays, which ds_a receives from s_c through different points on ds_b, do not all issue from one and the same element of s_c.

Since however the area of ds_b may be any whatever, nothing hinders us from supposing it so small, that it is an indefinitely small quantity of a higher order than ds_a. In this case, if the vertex of the pencil changes its position within ds_b, then the element of s_c which corresponds to ds_a will change its position through a distance so small that in comparison with the dimensions of the element it is indefinitely small and may be neglected. Hence in this case the element ds_c, which we obtain when we choose any point whatever p_b on element ds_b, and make it the vertex of the pencil of rays issuing from ds_a, may be considered as the part of ds_c which exchanges rays with ds_a through ds_b. The area of this element ds_c is easily found from what precedes. Let us suppose as before that a tangent plane to the surface s_b is drawn at p_b, and that tangent planes to the surfaces s_a and s_c are drawn at points on the elements ds_a and ds_c respectively; and let us consider the two latter elements as elements of the tangent planes. Take systems of co-ordinates on these three tangent planes, and form the quantities A and C, as given by the first and third of equations (I.). Then by equation (II.) we have

$$ds_c = \frac{C}{A} ds_a.$$

The quantity of heat which ds_c sends to ds_b, and which, as mentioned above, may be considered as the quantity which ds_a receives from the surface s_c through ds_b, is expressed by

$$e_c v_c^2 \frac{A}{\pi} ds_c ds_b;$$

or, substituting for ds_c its value given above,

$$e_c v_c^2 \frac{C}{\pi} ds_a ds_b.$$

If we compare this expression with that found above, which expresses the quantity of heat sent by ds_a through ds_b to s_c, we see that the two stand to each other in the ratio $e_a v_a^2 : e_c v_c^2$. If we now suppose that s_a and s_c are the surfaces of two perfectly black bodies of equal temperature, and make for such surfaces the assumption (which we have already seen to be necessary in the case of radiation without concentration), that the two products $e_a v_a^2$ and $e_c v_c^2$ are equal, then the quantities of heat given by the two expressions above are also equal.

§ 17. *Mutual Radiation of Entire Surfaces.*

If on the intermediate surface s_b we take, instead of the element hitherto considered, another element which is also supposed to be an indefinitely small quantity of a higher order, then the element of s_c, which exchanges rays with ds_a through this element of s_b, has a different position from that in the last case; but the two quantities of heat thus exchanged are again equal to each other; and the same holds of all other elements of the intermediate surface.

To obtain the quantity of heat which ds_a sends to s_c, not through a single element of the intermediate surface, but as a whole, and similarly the quantity of heat which as a whole it receives from s_c, we must integrate the two expressions found above over the surface s_b, so far as this surface is cut by the rays which pass from ds_a to s_c, and vice versâ. It is evident that if for each element of surface ds_b the two differentials are equal, then the whole integrals must also be equal.

Lastly, to find the quantities of heat, which the whole surface s_a exchanges with s_c, we must integrate both these expressions over the surface s_a. This process again will not disturb the equality, which exists for each of the separate elements ds_a.

Thus the principle previously discovered in a special case, viz. that two perfectly black bodies of equal temperatures exchange equal quantities of heat with each other, so far as the equation $e_a v_a^2 = e_c v_c^2$ holds for them, appears also as the result of an investigation, which in no way depends upon whether the rays issuing from s_a suffer a concentration at s_c, and vice versâ, or not; since the only condition was, that the rays issuing from s_a and s_c suffer no concentration at the intermediate surface s_b, a condition which may be always fulfilled, since this surface may be chosen at pleasure.

It follows further from this result that, if a given black body exchanges heat not only with one but with any number of black bodies, it receives from all of them exactly the same quantity of heat as it sends to them.

§ 18. *Consideration of Various Collateral Circumstances.*

The previous investigation has been made throughout under the assumption that any reflections and refractions take place without loss, or that there is no absorption of heat. We can, however, easily go on to shew that the results are not altered, if this condition is dropped. For consider any one of the different processes, by which a ray may be weakened on its way from one body to another; say that at a place where the ray cuts the boundary of two media, one part passes into the further medium by refraction, and the other is reflected. Then whether we consider the one part or the other as the continuation of the original ray, we have in both cases a weakened ray to deal with. The same holds if a ray be partially absorbed by entering a medium. But in each of these cases we have the law that two rays which traverse the same path in opposite directions are weakened in equal proportion. The quantities of heat, which two bodies mutually send to each other, are therefore weakened by such processes to the same extent; so that, if they would be equal without such weakening, they will also be equal when thus weakened. Another circumstance may be considered in connection with the processes above mentioned, viz. that a body may receive from the same direction rays which proceed from different bodies. For example, a body *A* may receive from a point, which lies on the bounding surface of two media, two rays coinciding in direction, but issuing from two different bodies *B* and *C*. One of these may come from the bounding medium and be refracted at the point, whilst the other is already in the bounded medium, and is reflected at the point. In this case, however, the two rays are weakened by refraction and reflection in such a way, that, if both were before of equal intensity, their sum afterwards is of the same intensity as either one of them had beforehand. Now suppose a ray of the same intensity to issue from the body *A* in the opposite direction, this will be divided, at the same point, into two parts, of which one enters the bounding medium, and passes forward to the body *B*, while the other is reflected and passes to the body *C*. The two parts which thus reach *B* and *C* from *A* are exactly as great as those which *A* receives from *B* and *C*. The body *A* thus stands to each of the bodies *B* and *C* in such a relation, that, assuming equal temperatures, it exchanges with them equal quantities of heat. The equality of the modifications which two rays undergo, when passing in opposite directions in any path whatever, must produce the same result in all other cases however complicated.

Again if, instead of perfectly black bodies, we consider such as only partially absorb the rays falling on them; or if instead of homogeneous heat we consider heat which contains systems of waves of different lengths; or lastly, if instead of taking all the rays as unpolarized we include the phenomena of polarization; still in all these cases we have to do only with facts, which hold equally for the heat sent out by any one body, and for that which it receives from other bodies. It is not necessary to consider these facts more closely, since they also take place with ordinary radiation without concentration, and the object of the present investigation was only to consider the special actions which might possibly be produced by concentration of the rays.

§ 19. *Summary of Results.*

The main results of this investigation may be briefly stated as follows:

(1) In order to bring the action of ordinary radiation, without concentration, into accordance with the fundamental principle, that heat cannot of itself pass from a colder to a hotter body, it is necessary to assume that the intensity of emission from a body depends not only on its own composition and temperature, but also on the nature of the surrounding medium; the relation being such, that the intensities of emission in different media stand in the inverse ratio of the squares of the velocities of radiation in the

media, or in the direct ratio of the squares of the coefficients of refraction.

(2) If this assumption as to the influence of the surrounding media is correct, the above fundamental principle is not only fulfilled in the case of radiation without concentration, but must also hold good when the rays are concentrated in any way whatever by reflections or refractions; since this concentration may indeed change the absolute magnitudes of the quantities of heat, which two bodies radiate to each other, but not the ratio between these quantities.

CHAPTER XIII.

DISCUSSIONS ON THE MECHANICAL THEORY OF HEAT AS HERE DEVELOPED, AND ON ITS FOUNDATIONS.

§ 1. *Different Views as to the Relation between Heat and Work.*

The papers of the author on the Mechanical Theory of Heat, as reproduced in all essential particulars in this volume, have frequently met with opposition; and it may be desirable to give here some of the discussions which have taken place on the question, since many points are raised in them, on which the reader may even yet be in doubt. The removal of these doubts may be facilitated by his learning what has been already written upon these points.

As already mentioned in Chapter III., the first important attempt to reduce to general principles the action of heat in doing work was made by Carnot. He started from the assumption that the total quantity of heat existing was invariable, and then supposed that the falling of heat from a higher to a lower temperature brought about mechanical work, in the same way as the falling of water from a higher to a lower level. But simultaneously with this conception the view gained ground that heat is a mode of motion, and that in producing work heat is expended. This view was set forth at intervals from the end of the last century by individual writers, such as Rumford, Davy, and Seguin*; but it was not till 1840 that the law corresponding to this view, viz. that of the equivalence of heat and work, was definitely laid down by Mayer and Joule, and proved by the latter to be correct by means of numerous and brilliant experiments. Soon afterwards the general principle of the conservation of energy was laid down by Mayer* and Helmholtz† (by the latter in a specially clear and convincing manner), and was applied to various natural forces.

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* In a paper by Mohr, published 1837, heat is in some places called a motion, in others a force.

A fresh starting point was thus given to researches on the science of heat; but in carrying these out great difficulties presented themselves, as was natural with so widely extended a theory, which was intertwined with all branches of natural science, and influenced the whole range of physical thought. In addition, the wide acceptation which Carnot's treatment of the mechanical action of heat had won for itself, especially after being brought by Clapeyron into an elegant analytical form, was unfavourable for the reception of the new theory. It was believed that there was no alternative but either to hold to the theory of Carnot, and reject the new view according to which heat must be expended to produce work, or conversely to accept the new view and reject Carnot's theory.

§ 2. *Papers on the Subject by Thomson and the Author.*

A very definite utterance on the then position of the question was given by the celebrated English physicist, now Sir William Thomson, in an interesting paper which he published in 1849 (when most of the above-mentioned researches of Joule had already appeared and were known to him), under the title, "An Account of Carnot's Theory of the Motive-Power of Heat, with numerical results deduced from Regnault's experiments on steam‡." He still maintains the position of Carnot, that heat may do work without any change in the quantity of heat taking place. He however points out a difficulty in this view, and goes on to say, p. 545: "It might appear that this difficulty might be wholly removed, if we gave up Carnot's fundamental axiom, a view which has been strongly urged by Mr Joule." He adds, "but if we do this we stumble over innumerable other difficulties, which are insuperable without the aid of further experimental researches, and without a complete reconstruction of the Theory of Heat. It is in fact experiment to which we must look, either for a confirmation of Carnot's axiom, and a clearing up of the difficulty which we have noticed, or for a completely new foundation for the Theory of Heat."

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* *Die organische Bewegung in ihrem Zusammenhange mit dem Stoffwechsel.* Heilbronn, 1845.

† *Ueber die Erhaltung der Kraft*, 18~~8~~47.

‡ *Trans. Royal Soc. of Edin.*, Vol. xvi. p. 541.

At the time when this paper appeared the author was writing his first paper "On the Mechanical Theory of Heat," which was brought before the Berlin Academy in 1850, and printed in the March and April numbers of Poggendorff's *Annalen*. In this paper he attempted to begin the reconstruction of the theory, without waiting for further experiments; and he succeeded, he believes, in overcoming the difficulties mentioned by Thomson, so far at least as to leave the way plain for any further researches of this character. He there pointed out the way in which the fundamental conception, and the whole mathematical treatment of heat, must be altered, if we accepted the principle of the equivalence of heat and work; and he further shewed that it was not needful wholly to reject the theory of Carnot, but that we might adopt a principle, based on a different foundation from Carnot's, but differing only slightly in form, which might be combined with the principle of the equivalence of heat and work, to form with it the ground-work of the new theory. This theory he then developed for the special cases of perfect gases and saturated vapour, and thereby obtained a series of equations, which have been universally employed in the form there given, and which will be found in Chapters II. and VI. of this volume.

§ 3. *On Rankine's Paper and Thomson's Second Paper.*

In the same month (February, 1850) in which the author's paper was read before the Berlin Academy, a valuable paper by Rankine was read before the Royal Society of Edinburgh, and was afterwards published in their *Transactions* (Vol. 20, p. 147)*.

Rankine there proposes the hypothesis, that heat consists in a rotary motion of the molecules; and thence deduces with much skill a series of principles on the action of heat, which agree with those deduced by the author from the first main principle of the mechanical theory*. The second main principle was not touched by Rankine in this paper, but was treated in a second paper, which was brought before the Royal Society of Edinburgh a year afterwards (April, 1851). In this he remarks† that he had at first felt doubtful of the correctness of the mode of reasoning by which the author had arrived at this second principle; but that having communicated his doubts to Sir W. Thomson, he was induced by him to investigate the subject more closely. He then found that it ought not to be treated as an independent principle in the theory of heat, but might be deduced from the equations, which he had given in the first section of his former paper. He proceeds to give this new proof of the principle, which however, as will be shewn further on, is in opposition, for certain very important cases, with his own views, as elsewhere expressed.

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* In 1854 it was reprinted with some alterations, in the *Phil. Mag.*, Series 4, Vol. VII. pp. 1, 111, 172.

This paper of 1851 Rankine added as a fifth section to his former paper on account of the connection between them. Thence has arisen with some authors the mistaken idea that this new paper was actually part of the former one, and that Rankine had therefore given a proof of the second main principle at the same time as the author. From the foregoing it will be seen that his proof (waiving the question how far it is satisfactory) appeared a year later than the author's.

In March of the same year, 1851, a second paper by Sir W. Thomson on the Theory of Heat was laid before the Royal Society of Edinburgh‡. In this paper he abandons his former position with regard to Carnot's theory and assents to the author's exposition of the second main principle. He then extends the treatment of the subject. For whilst the author had confined himself in the mathematical treatment of the question to the case of gases, of vapours, and of the process of evaporation, and had only added that it was easy to see how to make similar applications of the theory to other cases, Thomson developes a series of general equations, which are independent of the body's condition of aggregation, and only then passes on to more special applications.

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* *Edinb. Trans.*, Vol. xx. p. 205; *Phil. Mag.*, Series 4, Vol. VII. p. 249.

† *Phil. Mag.*, Vol. VII. p. 250.

‡ *Edin. Trans.*, Vol. xx. p. 261; *Phil. Mag.*, Series 4, Vol. IV. pp. 8, 105, 168.

On one point this second paper still falls short of the author's. For here also Thomson holds fast by the law of Mariotte and Gay-Lussac in the case of saturated vapour, and hesitates to accept an hypothesis with respect to permanent gases, which the author had made use of in his investigation (see Chapter II., § 2, of this work). On this he remarks*: "I cannot see that any hypothesis, such as that adopted by Clausius fundamentally in his investigations on this subject, and leading, as he shews, to determinations of the densities of saturated steam at different temperatures, which indicate enormous deviations from the gaseous laws of variation with temperature and pressure, is more probable, or is probably nearer the truth, than that the density of saturated steam does follow these laws, as it is usually assumed to do. In the present state of science it would perhaps be wrong to say that either hypothesis is more probable than the other." Some years later, after he had proved by his joint experiments with Joule that this hypothesis is correct within the limits assigned by the author, he used the same method as the author to determine the density of saturated vapour†.

Rankine and Thomson, so far as the author knows, have always recognized most frankly the position here assigned to the first labours of themselves and the author on the mechanical theory of heat. Thomson remarks in his paper‡: "The whole theory of the moving force of heat rests on the two following principles, which are respectively due to Joule and to Carnot and Clausius." Similarly he introduces the second main principle as follows: "Prop. II. (Carnot and Clausius)." He then proceeds to give a proof discovered by himself, and goes on§: "It is with no wish to claim priority that I make these statements, as the merit of first establishing the proposition on correct principles is entirely due to Clausius, who published his demonstration of it in the month of May last year, in the second part of his paper on the Motive Power of Heat."

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* *Edin. Trans.*, Vol. xx. p. 277; *Phil. Mag.*, Vol. IV. p. 111.

† *Phil. Trans.*, 1854, p. 321.

‡ *Edin. Trans.*, Vol. xx. p. 264; *Phil. Mag.*, Vol. IV. p. 11.

§ *Edin. Trans.*, Vol. xx. p. 266; *Phil. Mag.*, Vol. IV. pp. 14, 242.

§ 4. *Holtzmann's objections.*

From other quarters repeated and in some cases violent objections were raised to the author's first paper, to which, in the same and following years, a series of other papers, serving to complete the theory, were added. The earliest of these objections came from Holtzmann, who had published in 1845 a short pamphlet* on the subject. In this it would at first appear as if he wished to treat the question from the point of view, that for the generation of work there was necessary not merely a change in the distribution of heat, but also an actual destruction of it, and that conversely by destroying work heat could be again generated. He remarks (p. 7): "The action of the heat which has passed to the gas is thus either a raising of temperature, combined with an increase of the elastic force, or a certain quantity of mechanical work, or a mixture of the two; and a certain quantity of mechanical work is equivalent to the rise in temperature. Heat can only be measured by its effects; of the two above-named effects mechanical work is especially adapted for measurement, and it will be chosen accordingly for the purpose. I call a unit of heat that amount of heat, which by its entrance into a gas can perform the mechanical work a, or, using definite measures, which can raise a kilograms to a height of 1 metre." Further on (p. 12) he determines the numerical value of the constant a by the method previously used by Mayer, and explained in Chapter II., § 5; the number thus obtained corresponds perfectly with the mechanical equivalent of heat, as determined by Joule by various other methods. In extending his theory however, i.e. in developing the equations by which his conclusions are arrived at, he follows the same method as Clapeyron; so that he tacitly retains the assumption that the total quantity of heat which exists is invariable; and therefore that the quantity of heat which a body takes in, while it passes from a given initial condition to its present condition, must be expressible as a function of the variables, which determine that condition.

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* *Ueber die Wärme und Elasticität der Gase und Dämpfe;* von C. Holtzmann. Mannheim, 1845; also Pogg. *Ann.*, Vol. LXXII a.

In the author's first paper the inconsequence of this method was pointed out, and the question treated in another way; on which Holtzmann wrote an article*, in which he endeavoured to shew that this method of treatment, and specially the assumption that heat was expended in producing work, was inadmissible. The first objection which he raised was of a mathematical character. He carried out an investigation similar to that in the author's paper, in order first to determine the excess of the heat which a body takes in over that which it gives out, during a simple cyclical process consisting of indefinitely small variations, and secondly to compare this excess with the work done. But in such a process both the work done and the excess of heat must be indefinitely small quantities of the second order; and therefore in the whole investigation, care must be taken that all quantities of the second order, which do not cancel each other, shall be taken into account. This Holtzmann neglected to do; and he was thus led to a final equation, which contained a self-contradiction, and in which he therefore imagined that he had found a proof of the inadmissibility of the whole method. This objection was easily disposed of by the author in his reply.

He further brought forward as an obstacle to the theory, that, according to the formulæ given, the specific heat of a perfect gas must be independent of its pressure, whereas the experiments of Suermann, and also those of De la Roche and Bérard, shewed that the specific heat of gases increased as the pressure diminished. On this conflict between his own theory and the experiments which were then known and supposed to be correct, the author remarked in his reply as follows: "On this point I must first point out that, even if these observations are perfectly correct, they yet say nothing against the fundamental principle of the equivalence of heat and work, but only against the approximate assumption which I have made, viz. that a permanent gas, if it expand at constant temperature, absorbs only so much heat, as is required for the external work which it thus performs. But besides it is sufficiently known how unreliable are in general the determinations of the specific heats of gases; and all the more in those few observations which have been hitherto made at varying pressures. I did not therefore conceive myself bound to abandon the above assumption on account of these observations, although they were well known to me at the time when I wrote my former work; because the other grounds, which may be alleged *for* the correctness of the assumption within the limits which I had there laid down, are not wholly destroyed by the grounds which may be alleged *against* it."

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* Pogg. *Ann.*, Vol. LXXXII. p. 445.

This remark found its full confirmation in Regnault's *Researches,* published some years afterwards, on the specific heats of gases, which actually led to the result that these earlier observations were inaccurate, and that the specific heat of permanent gases is not visibly dependent on the pressure.

§ 5. *Decher's Objections.*

Another most energetic attack on the author's theory was made in 1858, by Professor G. Decher, in a paper "On the Nature of Heat," published in Dingler's *Polytechnischer Journal,* Vol. 148, pp. 1, 81, 161, 241. He characterizes the author's mathematics, in the first half of his paper of 1850, and in another paper of 1854, as an abuse of analysis, and bungling nonsense; he quotes the equations and principles there cited with single or double notes of admiration, and finally, after proving completely to his own satisfaction that the results are untenable, concludes thus: "These then are the data on which the fundamental principles of the new theory of Heat should rest, and by which its agreement with experience should be proved; they shew in the clearest light that the celebrated work of Herr Clausius, on which he himself and other physicists have built as on a secure foundation, is nothing more than a rotten nut, which looks well from the outside, but in reality contains nothing whatever."

Of the second half of the paper of 1850, which relates to the second main principle of the theory, Herr Decher observes (p. 163), that having mastered the first half, he saw no inducement to consider the second any further.

On examining more closely the objections raised by Herr Decher against the author's mathematical investigation, it is seen that they are due to the fact that he has not understood the differential equations there formed, which, though not generally integrable, become so as soon as one further relation is assumed to exist among the variables. In spite of all which the author has said, he has throughout treated the quantities to which these equations refer, viz. the quantities of heat taken in by a body in passing from a given initial condition to its present condition, as mere functions of the variables which determine the condition of the body. After quoting the author's equation for gases, viz.

$$\frac{d}{dt}\left(\frac{dQ}{dv}\right) - \frac{d}{dv}\left(\frac{dQ}{dt}\right) = A\frac{R}{v} \quad\text{..................(1)},$$

where A is the heat-equivalent of the unit of work, i.e. the reciprocal of E, he remarks, page 243: "In equation (1) $\left(\frac{dQ}{dv}\right)$ and $\left(\frac{dQ}{dt}\right)$ are fully determined as the differential coefficients of a known function of v and t, viz. Q, taken according to v and t respectively as sole variables; and in whatever way this function may be formed, and whatever relation may be supposed to exist between v and t, the right side of the equation must always equal zero."

This incorrect conception, thus formed by a professed mathematician, convinced the author that the meaning and treatment of this kind of differential equation, although long before established by Monge, was not so generally known as he had supposed; accordingly in his reply*, after a brief notice of some other points raised by Decher, he treated the subject more fully, giving a mathematical explanation, which seemed to him sufficient to obviate any such misunderstandings in future. This was afterwards prefixed to the collection of the author's papers as a mathematical introduction; and the essential part of it has been imported into the mathematical introduction to the present work.

§ 6. *Fundamental Principle on which the Author's Proof of the Second Main Principle rests.*

The more recent objections to the author's theory, and the departure from his views in more recent treatises, chiefly refer to his method of proving the second main principle of the theory. This proof rests, as shewn in Chapter III., on the following fundamental principle:—Heat cannot of itself (or without compensation) pass from a colder to a hotter body.

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* Dingler's *Polytechnischer Journal*, Vol. CL. p. 29.

This fundamental principle has been very variously received by the scientific public. Some appear to consider it so self-evident that it is needless to state it as a specific principle, whilst others on the contrary doubt its correctness.

§ 7. *Zeuner's first Treatment of the Subject.*

The first of the two modes of viewing the question mentioned in the last section appears in Zeuner's valuable paper of 1860 "On the Foundations of the Mechanical Theory of Heat." Here Zeuner gives the author's proof of the second main principle essentially in the same form as it has also been given by Reech*. The two differ only in one point. Reech gives the principle, that heat cannot of itself pass from a colder to a hotter body, expressly as a fundamental principle laid down by the author, and bases his proof upon it. Zeuner on the contrary does not mention this principle at all: he shews that if for any two bodies the second main principle of the theory did not hold, then by means of two cyclical processes performed with these two bodies in opposite directions, heat could be made to pass from a colder to a hotter body without any other special change, and he then goes on "as we may repeat both processes as often as we please, using the two bodies alternately in the way described, it would follow that we might, with the aid of nothing and without using either work or heat, continually transfer heat from a body of lower to one of higher temperature, which is an absurdity."

Few readers would probably assent to the opinion that the impossibility of transferring heat from a colder to a hotter body is so self-evident, as is here indicated by the short remark "which is an absurdity." Taking the facts of conduction, and of radiation under ordinary circumstances, we may undoubtedly say that this impossibility is established by daily experience. But even with radiation the question arises, whether it is not possible to concentrate the rays of heat artificially by means of mirrors or burning-glasses, so as to produce a higher temperature than that of the radiating bodies, and thus to effect the passage of the heat into a hotter body. The author has, therefore, thought it necessary to treat this question in a special paper, the contents of which are given in Chapter XII. Matters are still more complicated in cases when heat is transformed into work, and vice versâ, whether this be by effects such as those of friction, resistance of the air, and electrical resistances, or whether by the fact that one or more bodies suffer such changes of condition, as are connected partly with positive and partly with negative work, both internal and external. For by such changes heat, to use the common expression, becomes latent or free, as the case may be; and this heat the variable bodies may draw from or impart to other bodies of different temperatures.

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* *Récapitulation très-succincte des recherches algébriques faites sur la théorie des effects mécaniques de la chaleur par différents auteurs: Journ. de Liouville*, Ser. II. Vol. I. p. 58.

If for all such cases, however complicated the processes may be, it is maintained that without some other permanent change, which may be looked upon as a compensation, heat can never pass from a colder to a hotter body, it would seem that this principle ought not to be treated as one altogether self-evident, but rather as a newly-propounded fundamental principle, on whose acceptance or non-acceptance the validity of the proof depends.

§ 8. *Zeuner's later Treatment of the Subject.*

The mode of expression employed by Zeuner was criticized by the author on the grounds stated in the last section, in a paper published in 1863. In the second edition of his book, published in 1866, Zeuner has therefore struck out another way of proving the second main principle. Assuming the condition of the body to be determined by the pressure p and volume v, he forms for the quantity of heat dQ, taken in by the body during an indefinitely small variation, the differential equation

$$dQ = A\,(Xdp + Ydv) \ldots\ldots\ldots\ldots\ldots\ldots (2),$$

where X and Y are functions of p and v, and A is the heat-equivalent of work. This equation, as is well known, cannot be integrated so long as p and v are independent variables. He then proceeds (p. 41):

"But let S be a new function of p and v, the form of which may be taken for the present to be known as little as that of X and Y, but to which we will give a signification, which will appear immediately from what follows. Multiplying and dividing the right-hand side of the equation by S, we have

$$dQ = AS\left[\frac{X}{S}dp + \frac{Y}{S}dv\right] \text{..................(3).}$$

We may now choose S, so that the expression in brackets is a perfect differential; in other words, so that $\frac{1}{S}$ may be the integrating factor, or S the integrating divisor, of the expression within brackets of equation (2)."

From this it follows that in the following equation derived from (3),

$$\frac{dQ}{S} = A\left[\frac{X}{S}dp + \frac{Y}{S}dv\right] \text{..................(4),}$$

the whole right-hand side is a perfect differential, and therefore for a cyclical process we must have

$$\int\frac{dQ}{S} = 0 \text{..........................(5).}$$

In this way Zeuner arrives at an equation similar to equation (7) of Chapter IV., viz.

$$\int\frac{dQ}{\tau} = 0.$$

The resemblance, however, is merely external. The essence of this latter equation consists in this, that τ is a function of temperature only, and further a function which is independent of the nature of the body, and is therefore the same for all bodies. Zeuner's quantity S, on the contrary, is a function of both the variables, p and v, on which the bodies' condition depends; and further, since the functions X and Y, in equation (2), are different for different bodies, it must be true of S also that it may be different for different bodies. So long as this holds with regard to S, equation (5) has done nothing for the proof of the second main principle;

since it is self-evident that there must in general be an integrating factor, which may be denoted by $\frac{1}{S}$, and by which the expression within brackets in equation (2) may be converted into a complete differential. Accordingly, in Zeuner's proof, as he himself concludes, everything depends on the fact that S is a function of temperature only, and a function which is the same for all bodies, so that it may be taken as the true measure of the temperature.

For this purpose he supposes a body to undergo different variations, which are such that the body takes in heat whilst S has one constant value, and gives out heat whilst S has another constant value; and which together make up a cyclical process, shewing a gain or loss of heat. This procedure he compares with the lifting or dropping of a weight from one level to another, and with the corresponding mechanical work; and he proceeds (p. 68): "A further comparison leads to the interesting result that we may consider the function S as a length or a height, and the expression $\frac{Q}{AS}$ as a weight; in what follows therefore I shall call the above value the Weight of the Heat." Since a name has here been introduced for a magnitude containing S, in which name there is nothing which relates to the body under consideration, it appears that an assumption has here been tacitly made, viz. that S is independent of the nature of the body, which is by no means borne out by the earlier definition.

Zeuner then carries still further the comparison between the processes relating to gravity and those relating to heat, and transfers to the case of heat some of the principles which hold for gravity; in so doing he treats S as a height, and $\frac{Q}{AS}$ as a weight, just as before. Then, having finally observed that the principles thus obtained are true if we take S to mean the temperature itself, he proceeds (p. 74): "We are therefore justified in taking as the basis of our further researches the hypothesis that S is the true measure of temperature."

It appears from this that the only real foundation of the reasonings, which in his second edition Zeuner puts forward as the basis of the second main principle, is the analogy between the performance of work by gravity and by heat; and moreover that the point which has to be proved is in part tacitly assumed, in part expressly laid down as a mere hypothesis.

§ 9. *Rankine's Treatment of the Subject.*

We may now turn to those authors who have considered that the fundamental principle is not sufficiently trustworthy, or even that it is incorrect.

Here we must first examine somewhat more closely the mode of treatment which, as already mentioned, Rankine considered must be substituted for that of the author.

Rankine, like the author, divides the heat which must be imparted to the body, in order to raise its temperature, into two distinct parts. One of these serves to increase the heat actually existing in the body, and the other is absorbed in work. For the latter, which comprises the heat absorbed in the internal and in the external work, Rankine uses an expression, which in his first section he derives from the hypothesis that matter consists of vortices. Into this method of reasoning we need not enter further, since the circumstance that it rests on a particular hypothesis as to the nature of molecules and their mode of motion, makes it sufficiently clear that it must lead to the consideration of complicated questions, and thus leaves much room for doubt as to its trustworthiness. In the author's treatises he has based the development of his equations, not on any special views as to the molecular constitution of bodies, but only on fixed and universal principles; and thus, even if the above fact were the only one which could be alleged against Rankine's proof, the author would still expect his own mode of treating the subject to be finally established as the most correct. But yet more uncertain is Rankine's mode of determining the second part of the heat to be imparted, viz. that which serves to increase the heat actually existing in the body.

Rankine expresses the increase of the heat within the body, when its temperature t changes by dt, simply by the product Kdt, whether the volume of the body changes at the same time or not. This quantity K, which he calls the real specific heat, he treats in his proof as a quantity independent of the specific volume. Any sufficient ground for this procedure will be sought in vain in his paper; on the contrary, data are found which stand in direct opposition to it. In the introduction to his paper he gives, under equation (13), an expression for the real specific heat K, which contains a factor k, and of which he speaks as follows*: "The coefficient k (which enters into the value of the specific heat) being the ratio of the *vis viva* of the entire motion impressed on the atomic atmospheres by the action of their nuclei, to the *vis viva* of a peculiar kind of motion, may be conjectured to have a specific value for each kind of substance, depending in a manner yet unknown on some circumstance in the constitution of its atoms. Although it varies in some cases for the same substance in the solid, liquid, and gaseous states, there is no experimental evidence that it varies for the same substance in the same condition." Hence it appears to be Rankine's view that the real specific heat of the same substance may be different in different states of aggregation; and even for the assumption that it may be taken as invariable for the same state of aggregation he produces no other ground than that there is no experimental proof to the contrary.

In a later work, *A Manual of the Steam Engine and other Prime Movers*, 1859, Rankine speaks yet more distinctly on this point as follows (p. 307): "A change of real specific heat, sometimes considerable, often accompanies the change between any two of those conditions" (i.e. the three conditions of aggregation). How great a difference Rankine conceives to be possible between the real specific heats of one and the same substance in different states of aggregation, is shewn by his remark at the same place, that in the case of water the specific heat as determined by observation, which he calls the apparent specific heat, is nearly equal to the real specific heat. Now Rankine well knew that the observed specific heat for water is twice as great as that for ice, and more than twice as great as that for steam. Since then the real specific heat for ice and steam can never be greater than the observed, but only smaller, Rankine must assume that the real specific heat of water exceeds that of ice and steam by 100 per cent. or more.

If we now ask the question how on this supposition the increase of heat actually present in a body, which occurs when its temperature t increases by dt, and its volume v by dv, is to be expressed, the answer will be as follows: When the body, during its change of volume, suffers no change in its state of aggregation, we shall be able to express the increase of heat, as Rankine has done, by a simple product of the form Kdt; but the factor K must have different values for different states of aggregation. In cases, however, where the body during its change of volume also changes its state of aggregation (e.g. the case we have treated so often, where we have a certain quantity of matter partly in the liquid and partly in the gaseous condition, and where the magnitude of these two parts changes with the change in volume, either by the evaporation of part of the liquid, or by the condensation of part of the vapour), we can then no longer express the increase of heat connected with a simultaneous change in temperature and volume by a simple product Kdt; but must use an expression of the form

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* *Phil. Mag.*, Ser. 4, Vol. VII. p. 10.

$$Kdt + K_1 dv.$$

For if the real specific heat of a substance were different in different states of aggregation, it would be necessary to conclude that the quantity of heat existing in it must also depend on its state of aggregation; so that equal quantities of the substance in the solid, liquid, and gaseous condition would contain different amounts of heat. Accordingly, if part of the substance change its state of aggregation without any change of temperature, there must also be a change in the quantity of heat contained in the substance as a whole.

Hence it follows that Rankine by his own admission can only treat the mode in which he expresses the increase of heat, and the mode in which he uses that expression in his proof, as being allowable for the cases in which there are no changes in the state of aggregation; and, therefore, his proof holds for those cases only. For all cases where such changes occur the principle remains unproved; and yet these cases are of special importance, inasmuch as it is chiefly to these that the principle has hitherto been applied.

In fact we must go further, and say that the proof thus loses all strength even for cases where there is no change in the state of aggregation. If Rankine assumes that the real specific heat may be different in different states of aggregation, there seems no ground whatever left for supposing that it is invariable in the same state of aggregation. It is known that with solid and liquid bodies changes may occur in the conditions of cohesion, apart from any change in the state of aggregation. With gaseous bodies also, in addition to their great variations in volume, we have the distinction, that the more or less widely they are removed from their condensation-point the more or less closely do they follow the law of Mariotte and Gay-Lussac. How then, if changes in the state of aggregation may have an influence on the real specific heat, can we refuse to ascribe a similar, even if a smaller, influence to changes like the above? Thus the proposition, that the real specific heat is invariable in the same state of aggregation, is not only left unproved by Rankine, but, if we accept his special assumption, becomes in a high degree improbable.

To this criticism on his proof, which appeared in a paper of the author's, published in 1863[*], Rankine made no reply; but in a later article on the subject[†] he expressly maintained the truth of his view, frequently before stated, that the real specific heat of a body may be different in different states of aggregation; whereby the force of his proof is limited to the cases in which no change in the state of aggregation takes place.

§ 10. *Hirn's Objection.*

A yet more definite attack upon the author's fundamental principle, that heat cannot of itself pass from a colder to a hotter body, was made by Hirn in his work, published in 1862, *Exposition Analytique et Experimentale de la théorie mécanique de la chaleur*, and in two subsequent articles in *Cosmos*[‡]. He has there described a particular operation which gives at first sight an altogether startling result. After a reply from the author[§], he explained[‖] his attack as having for its object only to mark an apparent objection to the principle, whilst in reality he agreed with the author; and he has expressed himself to the same effect in the second and third editions of his valuable work.

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[*] Pogg. *Ann.*, Vol. cxx. p. 426.

[†] *Phil. Mag.*, Ser. 4, Vol. xxx. p. 410.

[‡] Vol. xxii. pp. 283, 412. [§] Vol. xxii. p. 560. [‖] Vol. xxii. p. 734.

In spite of this it seems worth while to state here the attack and the reply, because the conception of the subject there expressed is one very near the truth, and which might easily hold under other circumstances. An objection thus raised has a real scientific value of its own; and when it is put in so clear and precise a light, as Hirn has done in this case by means of his skilfully-conceived operation, it can only be advantageous for science: since the fact that the apparent objection is defined and placed clearly in view will greatly facilitate the clearing up of the point. In this way we shall attain the advantage that a difficulty, which otherwise might probably lead to many misunderstandings, and necessitate repeated and long discussions, will be disposed of once and for ever. In thus referring once more to this question, the author is far from wishing to make the objection a ground of complaint against Hirn, but rather believes that this objection has increased the debt which the Mechanical Theory of Heat owes to him on other accounts.

The operation alluded to, on which Hirn has based his observations, is as follows: Let there be two cylinders A and B (Fig. 32) of equal area, which are connected at the bottom by a comparatively narrow pipe. In each of these let there be an air-tight piston; and let the piston-rods be fitted with teeth engaging on each side with the teeth of a spur wheel, so that if one piston descends the other must rise through the same distance. The whole space below the cylinders, including the connecting pipe, must thus remain invariable during the motion, because as the space diminishes in one cylinder it increases in the other by an equal amount.

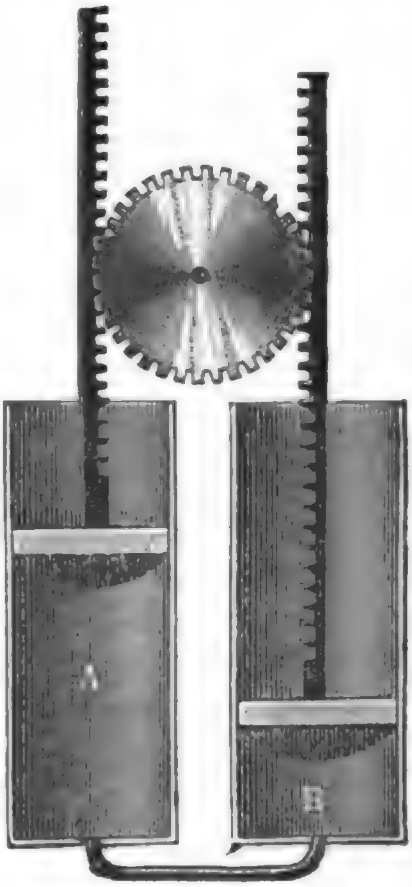

Fig. 32.

First, let us suppose the piston in B to be at the bottom, and therefore that in A at the top; and let cylinder A be filled with a perfect gas of any given density and of temperature t_0. Now let the piston descend in A, and rise in *B*, so that the gas is gradually driven out of *A* into *B*. The connecting pipe through which it must pass is kept at a constant temperature t_1, which is higher than t_0, so that the gas in passing is heated to temperature t_1, and at that temperature enters cylinder *B*. The walls of both cylinders, on the other hand, are non-conducting, so that within them the gas can neither receive nor give off heat, but can only receive heat from without as it passes through the pipe. To fix our ideas let the initial temperature of the gas be that of freezing, or 0°, and that of the connecting pipe 100°, the pipe being surrounded by the steam of boiling water.

It is easy to see what will be the result of this operation. The first small quantity of gas which passes through the pipe will be heated from 0° to 100°, and will expand by the corresponding amount, i.e. $\frac{100}{273}$ of its original volume. By this means the gas which remains in *A* will be somewhat compressed, and the pressure in both the cylinders somewhat raised. The next small quantity of gas which passes through the pipe will expand in the same way, and will thereby compress the gas in both cylinders. Similarly each successive portion of gas will act to compress still further not only the gas left in *A*, but also the gas which has previously expanded in *B*, so that the latter will continually tend to approach its initial density. This compression causes a heating of the gas in both cylinders; and as all the gas which enters *B* enters at a temperature of 100°, the subsequent temperature must rise above 100°, and this rise must be the greater, the more the gas within *B* is subsequently compressed.

Let us now consider the state of things at the end of the operation, when all the gas has passed from *A* into *B*. In the topmost layer, just under the piston, will be the gas which entered first, and which, as it has suffered the greatest subsequent compression, will be the hottest. The layers below will be successively less hot down to the lowest, which will have the same temperature, 100°, which it attained in passing the pipe. For our present purpose there is no need to know the temperature of each separate layer, but only the mean temperature of the whole, which is equal to the temperature that would exist if the temperatures in the different layers were equalized by a mixing up of the gas. This mean temperature will be about 120°.

In a later article published in *Cosmos,* Hirn has completed this operation, by supposing that the gas in *B* is finally brought into contact with mercury at 0°, and thereby cooled back again to 0°; that it is then driven back from *B* to *A* under the same conditions as from *A* to *B,* and is therefore heated in the same manner; that it is then again cooled by mercury, again driven from *A* to *B,* and so on. Thus we have a periodical operation, in which the gas is continually brought back to its original condition, and all the heat given off by the source of heat passes over to the mercury employed for cooling. Here we will not enter into this extension of the process, but confine ourselves to the first simple operation, in which the gas is heated from 0° to a mean temperature of 120°; for this operation comprises the essence of Hirn's objection.

In this operation it is clear that no heat is gained or lost; for the pressure in both cylinders is always equal, and therefore both pistons are always pressed upwards with equal force. These forces are communicated to the wheel which gears with the piston-rods; and thus, neglecting friction, an indefinitely small force will be sufficient to turn the wheel in one or the other direction, and thereby move one piston up and the other down. The excess of heat in the gas cannot therefore be created by external work.

The process, as is easily seen, is as follows. Whilst a quantity of gas, which is a very small fraction of the whole, is heated and expanded in passing through the pipe, it must take in from the source sufficient heat to heat it at constant pressure. Of this, one part goes to increase the heat actually existing in the gas, and another part to do the work of expansion. But since the expansion of the gas within the pipe is followed by a compression of the gas within the cylinders, the same quantity of heat will be generated in the one place as is absorbed in the other. Thus that part of the heat derived from the source, which is turned into work within the pipe, appears again as heat within the cylinders; and serves to heat the gas left in *A* above 0°, its initial temperature, and the gas which has passed into *B* above 100°, the temperature at which it entered; in other words to produce the rise in temperature already mentioned. Accordingly, without considering the intermediate process, we may say that all the heat, which the gas contains at the end of the operation more than at the beginning, comes from the source of heat attached to the connecting-pipe. Hence we have the singular result, that by means of a body whose temperature is 100°, i.e. the steam surrounding the pipe, the gas within the cylinders is heated above 100°, or, looking only to the mean temperature, to 120°. Here then, is a contradiction of the fundamental principle that heat cannot of itself pass from a colder to a hotter body, inasmuch as the heat imparted by the steam to the gas has passed from a body at 100° to a body at 120°.

One circumstance however has been forgotten. If the gas had had an initial temperature of 100° or more, and had then been raised to a still higher temperature by steam, whose temperature was only 100°, this would no doubt be a contradiction of the fundamental principle. But this is not the real state of things. In order that the gas may be above 100° at the end of the operation, it must necessarily be below 100° at the beginning. In our example, in which the final temperature is 120°, the initial is 0°. The heat, which the steam has imparted to the gas, has therefore served in part to heat it from 0° to 100°, and in part to raise it from 100° to 120°. But the fundamental principle refers only to the temperatures of the bodies between which heat passes, as they are at the exact moment of the passage, and not as they are at any subsequent time. Accordingly we must conceive the passage of heat in this operation to take place as follows. The one part of the heat given off by the steam has passed into the gas, whilst its temperature was still below 100°, and has therefore passed into a colder body; and only the other part, which has served to heat the gas beyond 100°, has passed into a hotter body. If then we compare this with the fundamental principle, which says that, when heat passes from a colder to a hotter body, without any transformation of work into heat or any change in molecular arrangement, then of necessity there must be in the same operation a passage of heat from a hotter to a colder body, we easily see that there is complete agreement between them. The peculiarity in Hirn's operation is only this, that there are not two different bodies concerned, of which one is colder and the other hotter than the source of heat; but one and the same body, the gas, takes in one part of the operation the place of the colder, and in another part that of the hotter body. This involves no departure from the principle, but is only one special case out of the many which may occur. Dupré has raised similar objections against the fundamental principle; but as there is nothing in them essentially new, they will not here be entered upon.

§ 11. *Wand's Objections.*

Some years later Th. Wand treated of the same principle in a paper entitled "Kritische Darstellung des zweiten Satzes der Mechanische Wärmetheorie*." He gives his conclusions in the three propositions following: (1) "The second principle of the mechanical theory of heat, i.e. the impossibility of a passage of heat to a higher temperature without a conversion into work or a corresponding passage of heat to a lower temperature, is false." (2) "The deductions from this principle are only approximate empirical truths, which hold only so far as they are established by experiment." (3) "For technical calculations the principle may be taken as correct, since experiments on the substances used for the generation of work and of cold shew a very close agreement with it."

The placing of such propositions side by side seems in itself a doubtful measure. If a principle has been found to agree with fact in so many cases, as to compel us to say that for technical calculations it may be taken as correct, it seems dangerous to conclude nevertheless that it is false, in the face of the probable supposition that the apparent objections which yet remain would be cleared up by closer examination.

The following appear to be the chief grounds on which Wand bases his rejection of the principle; excluding those which relate to internal work and electrical phenomena, because these subjects are not here treated of.

"If we suppose," he says on p. 314, "that in the bringing of a certain quantity of heat from a lower to a higher temperature a certain quantity of work must of necessity be destroyed, it follows that, if the same quantity of heat falls from a higher to a lower temperature, the same quantity of work must re-appear. Now suppose that this fall takes place by simple conduction or by a non-reversible cyclical process. Then the above is not true, because the falling of heat by conduction goes on without any other change whatever. Therefore for equalizations of temperature by simple conduction there is nothing equivalent to the second principle; and this from the logical point of view is one of the weakest points in that principle, and leads to much subsequent inconvenience." The circumstance here mentioned, that compensation is required only in the passage of heat to a higher temperature, and not to a lower, has been frequently stated above; and in Chapter X. is expressed in the general form, that negative transformations cannot take place without positive, but that positive transformations can take place without negative. From this circumstance the second main principle becomes doubtless less simple in form than the first, but it would be hard to shew that it is logically imperfect.

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* Karl's *Repertorium der Experimental-Physik*, Vol. IV. pp. 281, 369.

The inconveniences mentioned by Wand in the above paragraph he arrives at by the following considerations. He supposes a simple cyclical process to be carried out, during which the two bodies between which the heat passes, and which he calls the heating and cooling body, have temperatures which are close to 0°, and differ from each other by an indefinitely small quantity, which he calls *dt*. For this symbol, which will appear with another signification in the analysis which follows, we will substitute δ, and will call the temperatures of the two bodies, reckoned from freezing-point, 0 and δ respectively. Further, Wand supposes the cyclical process to be so arranged, that one unit of heat passes over from the hotter to the colder body, and therefore that the quantity of heat $\frac{\delta}{273}$ is transformed into work. He then proceeds: "The process being ended, I will heat the whole apparatus, comprising both the heating and the cooling body, by 100°. The difference of temperature between the two bodies will remain unaltered. If we now wish to destroy the heat thus obtained by means of the reverse cyclical process, we must take from the colder body the heat $\frac{373}{273}$. The colder body thus loses the heat $\frac{100}{273}$, and gives it up to the hotter body; and if by the reverse process all is cooled back again to the initial temperature 0°, the initial condition of things is restored. There is no work performed or consumed, and yet a passage of heat has taken place from the second body, which has remained the colder, to the first which has remained the hotter throughout the process. This however is no refutation of the second principle. For to obtain this result there must be a continuous succession of alternate heatings and coolings of the apparatus, i.e. heat must pass from a hotter to a colder body; but this passage takes place by conduction, for which there is no equivalent. Hence it follows from the process here described, that with regard to the distribution of the heat it is by no means the same thing, whether we do nothing at all, or carry out a compound cyclical process as here described."

We have here the case of two opposite cyclical processes carried out at different temperatures, in which the work done and the work consumed cancel each other, but more heat passes from the hotter to the colder body than vice versâ; and Wand holds that the passage of the surplus heat from the colder to the hotter body has taken place without compensation. He has however neglected certain differences of temperature, which occur in this somewhat complicated operation. For after the first process, in which the hotter body has given off and the colder body taken in heat, he heats the whole apparatus and the two bodies by 100°; and he cools them by 100° after the second process, in which the colder body has given off heat and the hotter taken it in. But in giving off and taking in heat the two bodies alter their temperature somewhat, and the reservoirs of heat, which perform the heating and cooling, do not therefore take back the heat during the cooling at the same temperature as they gave it out during the heating. Hence arise passages of heat of which Wand has taken no account.

These differences of temperature are of course very small, since the two bodies must be assumed so large, that the variations of temperature produced in them by the cyclical process may remain small compared to the difference of the original temperatures. But then the quantities of heat, which the bodies take from and give back to the reservoirs during their heating and cooling, are also very large; and since to determine the heat which has passed we must multiply the differences of temperature by the actual quantities of heat, we arrive at magnitudes which are quite large enough to compensate for the surplus heat which has passed between the bodies.

To prove this point we will make the calculation itself. First, with regard to the actual surplus heat which has passed between the bodies, since the temperatures are 0 and δ, and the quantity of heat equals $\frac{100}{273}$, this has the equivalence value $\frac{100}{273}\left(\frac{1}{273+\delta}-\frac{1}{273}\right)$ or, neglecting terms of a higher order than the first with regard to δ, $-\frac{100}{273^3}\delta$. We have now to determine the equivalence value of the passages of heat, which take place during the heating and cooling of the body by 100°. By Chapter IV., § 5, we must divide the element of heat taken in by one of the two bodies from a reservoir of heat (reckoning heat given off as negative heat taken in) by the absolute temperature which the body has at the moment, and we must then form the negative integral for the heating and cooling.

Let M be the mass of each body, and C its specific heat, which we suppose constant; then the quantity of heat, which it takes in during a rise of temperature dt, equals $MCdt$, and this we shall take as expressing the element of heat. If for convenience we put

$$\epsilon=\frac{1}{MC} \quad \text{.........................(6)},$$

the element will be expressed by $\frac{1}{\epsilon}dt$. We must consider MC as very large, and therefore ϵ as very small, so much so as to be small even in comparison with the small difference of temperature δ.

If we now take the first cyclical process, the colder body has, to begin with, the temperature 0, and the hotter the temperature δ. During the process the former takes in the quantity of heat 1, and the latter loses the quantity $1+\frac{\delta}{273}$. These must be divided by MC, or multiplied by ϵ, to obtain the changes of temperature which they produce in the bodies; thus at the end of the process the colder body has the temperature ϵ, and the hotter the temperature

$$\delta-\left(1+\frac{\delta}{273}\right)\epsilon.$$

From these temperatures both bodies are now to be heated by 100°.

The negative integral relating to the heating of the colder body is

$$A=-\int_{\epsilon}^{100+\epsilon}\frac{\frac{1}{\epsilon}\,dt}{273+t}.$$

If we put $\tau=t-\epsilon$, then

$$A=-\int_{0}^{100}\frac{\frac{1}{\epsilon}\,d\tau}{273+\tau+\epsilon}.$$

Neglecting higher terms in the expansion of ϵ, we have

$$\frac{1}{273+\tau+\epsilon}=\frac{1}{273+\tau}-\frac{\epsilon}{(273+\tau)^2},$$

whence $$A=-\frac{1}{\epsilon}\int_0^{100}\frac{d\tau}{273+\tau}+\int_0^{100}\frac{d\tau}{(273+\tau)^2}\ldots\ldots(7).$$

The negative integral relating to the heating of the hotter body is

$$B=-\int_{\delta-\left(1+\frac{\delta}{273}\right)\epsilon}^{100+\delta-\left(1+\frac{\delta}{273}\right)\epsilon}\frac{\frac{1}{\epsilon}\,dt}{273+t}.$$

Whence we obtain in the same way as before

$$B=-\frac{1}{\epsilon}\int_{\delta}^{100+\delta}\frac{d\tau}{273+\tau}-\left(1+\frac{\delta}{273}\right)\int_{\delta}^{100+\delta}\frac{d\tau}{(273+\tau)^2}\ldots\ldots(8).$$

During the second cyclical process the colder body gives off a quantity of heat $=\frac{373}{273}$, and the hotter body receives a quantity $\frac{373}{273}+\frac{\delta}{273}$. The temperatures of the two bodies, after the second cyclical process, become respectively

$$100+\epsilon-\frac{373}{273}\epsilon=100-\frac{100}{273}\epsilon,$$

$$100+\delta-\left(1+\frac{\delta}{273}\right)\epsilon+\left(\frac{373}{273}+\frac{\delta}{273}\right)\epsilon=100+\delta+\frac{100}{273}\epsilon.$$

From these temperatures both bodies are cooled down by 100°. The negative integral relating to this cooling is for the colder body

$$C=-\int_{100-\frac{100}{273}\epsilon}^{-\frac{100}{273}\epsilon}\frac{\frac{1}{\epsilon}\,dt}{273+t}=\int_{-\frac{100}{273}\epsilon}^{100-\frac{100}{273}\epsilon}\frac{\frac{1}{\epsilon}\,dt}{273+t};$$

whence as before we have

$$C=\frac{1}{\epsilon}\int_0^{100}\frac{d\tau}{273+\tau}+\frac{100}{273}\int_0^{100}\frac{d\tau}{(273+\tau)^2}\;\ldots\ldots\ldots(9).$$

For the cooling of the hotter body we have similarly

$$D=\frac{1}{\epsilon}\int_{\delta}^{100+\delta}\frac{d\tau}{273+\tau}-\frac{100}{273}\int_{\delta}^{100+\delta}\frac{d\tau}{(273+\tau)^2}\;\ldots.(10).$$

By adding together A, B, C, D, we obtain the equivalence value of all the transferences of heat during the heating and cooling. In this addition the integrals which have the factor $\frac{1}{\epsilon}$ cancel each other, and two of the others may be combined together. Whence we have

$$A+B+C+D=\frac{373}{273}\int_0^{100}\frac{d\tau}{(273+\tau)^2}$$

$$-\left(\frac{373}{273}+\frac{\delta}{273}\right)\int_{\delta}^{100+\delta}\frac{d\tau}{(273+\tau)^2}\;\ldots\ldots\ldots(11).$$

Performing the integration, the right-hand side becomes

$$\frac{373}{273}\left(-\frac{1}{373}+\frac{1}{273}\right)-\left(\frac{373}{273}+\frac{\delta}{273}\right)\left(-\frac{1}{373+\delta}+\frac{1}{273+\delta}\right).$$

If we expand the second product in terms of δ to the first order, most of the resulting terms cancel each other, and the expression for the equivalence value of the transferences of heat during the heating and cooling becomes finally

$$\frac{100}{(273)^3}\,\delta.$$

This expression fulfils the condition of being equal and opposite to the equivalence value of the surplus heat actually transferred between the two bodies. This transfer therefore is not uncompensated, but fully compensated as the second principle requires. We thus see that the operation suggested by Wand does not give the smallest ground for objecting to the principle.

Another objection is drawn by Wand from the following considerations. He proposes the question whether the principle can be derived by mechanical reasoning from the ideas which we can form of the nature and action of heat. With this object he first applies the hypothesis maintained by the author and others as to the molecular motion of gaseous bodies, and finds that this does actually lead to the principle in question. He then says that it is not sufficient to prove that one particular hypothesis leads to the principle, but that all possible mechanical hypotheses on the nature of heat must be shewn to lead to it. Accordingly as a second example he takes another hypothesis, which he conceives specially adapted to represent the phenomena of expansion, and of the increase of pressure by heat. On this hypothesis a row of elastic balls, any two of which are connected by an elastic spring, vibrate in such a way that all of them are in similar phases. From this hypothesis he arrives at an equation different from that which he has chosen as the criterion of the second principle, and then draws the conclusion, "the second principle cannot therefore be universally derived from the principles of mechanics." But upon such a conclusion the question may be asked, whether in reality the hypothetical motion, which he supposes, agrees with the actual motion, which we call heat, in such a way that the same equations must hold for both. So long as this is not proved the conclusion cannot be considered to be made out.

Finally, Wand considers the process which occurs in nature, when in the growth of plants, under the influence of the sun's rays of light and heat, carbonic acid and water are absorbed, and oxygen liberated; whilst the organic substances thus formed, if afterwards burnt or serving as nourishment to animals, unite themselves again with oxygen to form carbonic acid and water, and thereby generate heat. This transformation of the sun's heat he considers to be in flat contradiction to the second principle. To the analysis which he gives many objections might be taken; but the author considers that a process in which so much is still unknown, as that of the growth of plants under the influence of the sun, is altogether unfit to be used as a proof either for or against the principle in question.

§ 12. *Tait's Objections.*

Finally the author has to mention certain objections recently raised against his theory by Tait; objections which have surprised him equally by their substance and by their form. In an article which appeared in 1872 on the History of the Mechanical Theory of Heat[*], the author had observed, that Tait's work, *A sketch of Thermodynamics*, no doubt owed its existence chiefly to the wish of claiming the Mechanical Theory of Heat as far as possible for the English nation;—a supposition for which the clearest grounds can be adduced. Further on in the article he had observed that Tait had ascribed to Sir William Thomson a formula due to the author, and had quoted it as given by Thomson in a paper which contained neither the formula itself nor anything equivalent to it. The author expected that Mr Tait, in answering this article, would specially address himself to these two points, of which the latter particularly required clearing up. A reply appeared indeed[†], and one written in a very acrimonious tone; but to the author's surprise these two points were nowhere touched upon, a different turn being given to the whole matter. For whilst in the work previously alluded to the author's researches on the Mechanical Theory of Heat, even if in his own view they were not put in their right relation to those of English writers, were yet described at great length and with a general recognition of their merit, their correctness was here at once assailed, by the declaration that the fundamental principle, that heat cannot of itself pass from a colder to a hotter body, is untrue.

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[*] Pogg. *Ann.*, Vol. CXLV. p. 132.

[†] *Phil. Mag.*, Series 4, Vol. XLIII.

To prove this two phenomena relating to electric currents are adduced. But in a rejoinder published shortly afterwards* the author was easily able to prove that these phenomena in no way contradict the principle, and that one of them is even so evidently in accordance with it, that it may serve as an example specially adapted to illustrate and establish it. As electrical phenomena are not here treated of, this is not the place to enter further into this subject.

Tait further observed in his reply, that by the author's introduction of what he named Internal Work and Disgregation, he had done a serious injury to science, offering however nothing to support this, beyond the brief remark: "In our present ignorance of the nature of matter such ideas can do only harm." What Tait has to object to the conception of internal work, it is difficult to understand. In his first paper on the Mechanical Theory of Heat the author divided the work during the body's change of condition into External and Internal Work, and shewed that those two quantities of work differed essentially in their mode of action. Since that time this distinction has been similarly made by all writers, so far as he is aware, who have treated of the Mechanical Theory of Heat.

As regards the method (which will be described on a future occasion) of calculating the combined internal and external work, and the conception of disgregation introduced by the author with this object, purely mechanical investigations have recently led to an equation, exactly corresponding with that which the author proposed in the science of heat, and in which the disgregation makes its appearance. If these investigations cannot yet be considered as complete, they nevertheless shew, at least in the author's opinion, that the nature of things requires the introduction of this conception.

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* *Phil. Mag.*, Series 4, Vol. XLIII.

He therefore leaves the objections of Tait, with as much confidence as those of Holtzmann, Decher, and others, to the good judgment of the reader*.

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* For a rejoinder by Prof. Tait to these observations, see *Sketch of Thermodynamics*, 2nd edition, 1877, p. xv.

FINIS.

APPENDIX I.

ON THE THERMO-ELASTIC PROPERTIES OF SOLIDS.

Sir William Thomson was the first who examined the thermo-elastic properties of elastic solids. Instead of abstracting his investigation (*Quarterly Mathematical Journal*, 1855) it may be well to present the subject as an illustration of the method of treatment by the Adiabatic Function.

Consider any homogeneously-strained elastic solid. To define the state of the body as to strain six quantities must be specified, say u, v, w, x, y, z: these are generally the extensions along three rectangular axes, and the shearing strains about them, each relative to a defined standard temperature and a state when the body is free from stress. The work done by external forces when the strains change by small variations may always be expressed in the form

$$(U\delta u + V\delta v + \ldots) \times \text{volume of the solid},$$

because the conditions of strain are homogeneous. U, V ...... are the stresses in the solid: each is a function of uv ...... and of the temperature, and is determined when these are known. Let θ denote the temperature (where θ is to be regarded merely as the *name* of a temperature, and the question of how temperatures are to be measured is not prejudged).

Amongst other conditions under which the strains of the body may be varied, there are two which we must consider. First, suppose that the temperature is maintained constant; or that the change is effected *isothermally*. Then θ is constant. Secondly, suppose that the variation is effected under such conditions that no heat is allowed to pass into or to leave the body; or that the change is effected *adiabatically*. In the latter case $\theta, u, v,$ ...... are connected by a relation involving a parameter which is always constant when heat does not pass into or out of the solid: this parameter is called the *adiabatic function.*

We have now fourteen quantities relating to the body, viz. six elements of strain, six of stress, the quantity θ which defines the temperature, and the parameter ϕ the constancy of which imposes the adiabatic condition. Any seven of these may be chosen as independent variables.

Let the body now undergo Carnot's four operations as follows:—

1°. Let the stresses and strains vary slightly under the sole condition that the temperature does not change. Let the consequent increase of ϕ be $\delta\phi$. Heat will be absorbed or given out, and, since the variations are small, the quantity will be proportional to $\delta\phi$, say

$$f(\theta, u, v, w, \ldots\ldots)\,\delta\phi.$$

2°. Let the stresses and strains further vary adiabatically, and let $\delta\theta$ be the consequent increase of temperature.

3°. Let the stresses and strains receive any isothermal variation, such that the parameter ϕ returns to its first value. Heat will be given out or absorbed, equal to

$$(f+\delta f)\,\delta\phi.$$

4°. Let the body return to its first state.

Here we have a complete and reversible cycle. The quantity of heat given off $\delta f \times \delta\phi$ is equal to the work done by external forces. Now Carnot's theorem (or the Second Principle of Thermodynamics) asserts that the work done, or $\delta f \times \delta\phi$, divided by the heat transferred from the lower to the higher temperature, $f \times \delta\phi$, is equal to a function of θ only (which function is the same for all bodies) multiplied by $\delta\theta$. Thus

$$\frac{\delta f}{f} = F(\theta)\,\delta\theta,$$

$$\log(f) = \int F\theta\, d\theta + \text{a function of } \phi\,;$$

the function of ϕ being added because the variation was performed under the condition that ϕ was constant. By properly choosing the parameter ϕ this function may be included in $\delta\phi$, and we have, as the quantity of heat absorbed in the first operation,

$$\epsilon^{\int F\theta d\theta} \times \delta\phi.$$

The mode of measuring temperature being arbitrary, we shall find it convenient to define that temperature is so measured that $F(\theta) = \frac{1}{\theta}$; then we have :—

$$\text{Heat absorbed in first operation} = \theta\delta\phi \ldots\ldots\ldots\ldots\ldots (1);$$

$$\text{Work done by external forces} = \delta\theta \times \delta\phi \ldots\ldots\ldots\ldots (2).$$

We must now examine more particularly the variations in the stresses and strains. Denote the values of U, V, ..., u, v, ... by different suffixes for the four operations.

The work done by the external forces in these operations is respectively

$$\frac{U_1 + U_2}{2}(u_2 - u_1) + \frac{V_1 + V_2}{2}(v_2 - v_1) + \&c.,$$

$$\frac{U_2 + U_3}{2}(u_2 - u_3) + \frac{V_2 + V_3}{2}(v_3 - v_2) + \&c.,$$

$$\frac{U_3 + U_4}{2}(u_4 - u_3) + \frac{V_3 + V_4}{2}(v_4 - v_3) + \&c.,$$

$$\frac{U_4 + U_1}{2}(u_1 - u_4) + \frac{V_4 + V_1}{2}(v_1 - v_4) \div \&c.;$$

and the sum of these is equal to $\delta\phi\,\delta\theta$.

Hence a variety of important relations may be obtained.

Let all the strains but one be constant: then we have

$$u_2 = u_1 + \frac{du}{d\phi}\,d\phi,$$

$$u_3 = u_2 + \frac{du}{d\theta}\,d\theta,$$

$$u_4 = u_3 - \frac{du}{d\phi}\,d\phi,$$

$$u_1 = u_4 - \frac{du}{d\theta}\,d\theta,$$

with similar equations for U_2, &c. Hence the Work done in the successive operations is,

$$\frac{U_1 + U_2}{2} \times \frac{du}{d\phi} d\phi,$$

$$\frac{U_2 + U_3}{2} \times \frac{du}{d\theta} d\theta,$$

$$-\frac{U_2 + \frac{dU}{d\theta} d\theta + U_1 + \frac{dU}{d\theta} d\theta}{2} \times \frac{du}{d\phi} d\phi,$$

$$-\frac{U_2 - \frac{dU}{d\phi} d\phi + U_3 - \frac{dU}{d\phi} d\phi}{2} \times \frac{du}{d\theta} d\theta.$$

Adding these, the total Work done becomes

$$\left(-\frac{du}{d\phi}\frac{dU}{d\theta} + \frac{du}{d\theta}\frac{dU}{d\phi}\right) \times d\theta d\phi,$$

the differentiations being performed when u and U are expressed as functions of θ, ϕ and the five other strains.

The same is true if five stresses are constant, that is if u and U are expressed as functions of θ, ϕ and the five other stresses.

But from (2) the Work done $= d\theta \times d\phi$. Hence it follows generally (using the well-known theorem as to Jacobians) that

$$\frac{d\phi}{dU}\frac{d\theta}{du} - \frac{d\phi}{du}\frac{d\theta}{dU} = 1 \quad \text{.................... (3)},$$

ϕ and θ being expressed as functions of u, U; and either the five other stresses or the five other strains being constant.

These equations are still true if the independent variables are partly stresses and partly strains, so long as no two are of the same name: e.g. if they are $vwXYZ$.

From equation (3) all the thermo-elastic properties of bodies may be deduced. We have generally

$$d\theta = \frac{d\theta}{dU} dU + \frac{d\theta}{du} du \quad \text{.......................(4)},$$

$$d\phi = \frac{d\phi}{dU} dU + \frac{d\phi}{du} du \quad \text{.......................(5)}.$$

Putting $d\phi = 0$, we have

$$\frac{dU}{du}\text{ (when }\phi\text{ is constant)} = -\frac{\dfrac{d\phi}{du}}{\dfrac{d\phi}{dU}}.$$

Putting $d\theta = 0$, we have

$$\frac{dU}{du}\text{ (when }\theta\text{ is constant)} = -\frac{\dfrac{d\theta}{du}}{\dfrac{d\theta}{dU}}.$$

Let $\frac{d_\phi\theta}{du}$ denote $\frac{d\theta}{du}$ under the condition that ϕ is constant, that is, where θ is expressed as a function of ϕu instead of Uu. Then by (4)

$$\frac{d_\phi\theta}{du} = \frac{d\theta}{dU}\frac{dU}{du} + \frac{d\theta}{du} = -\frac{d\theta}{dU} \times \frac{\dfrac{d\phi}{du}}{\dfrac{d\phi}{dU}} + \frac{d\theta}{du}$$

$$= -\frac{1}{\dfrac{d\phi}{dU}},\text{ by (3).}$$

This is the fourth thermodynamic relation (see *Maxwell on Heat*, 1877, p. 169).

The others are obtained in a similar way thus:—

$$\frac{d_\phi\theta}{dU} = \frac{d\theta}{dU} - \frac{d\theta}{du}\,\frac{\dfrac{d\phi}{dU}}{\dfrac{d\phi}{du}} = -\frac{1}{\dfrac{d\phi}{du}} = -\frac{d_U u}{d\phi},$$

$$\frac{d_\theta\phi}{du} = \frac{d\phi}{du} - \frac{d\phi}{dU}\,\frac{\dfrac{d\theta}{du}}{\dfrac{d\theta}{dU}} = -\frac{1}{\dfrac{d\theta}{dU}} = -\frac{d_u U}{d\theta},$$

$$\frac{d_\theta\phi}{dU} = \frac{d\phi}{dU} - \frac{d\phi}{du}\,\frac{\dfrac{d\theta}{dU}}{\dfrac{d\theta}{du}} = \frac{1}{\dfrac{d\theta}{du}} = \frac{d_U u}{d\theta}.$$

These relations are true provided each of the other strains, or else its corresponding stress, is constant.

Take the last of these for interpretation. When θ is constant we have by (1),

$$\text{Heat absorbed in any change (or } dq) = \theta d\phi.$$

Hence
$$\frac{d_\theta \phi}{dU} = \frac{1}{\theta} \frac{dq}{dU};$$

or, by the fourth relation,

$$\frac{d_U \phi}{d\theta} = \frac{1}{\theta} \frac{dq}{dU}.$$

Here $\frac{d_U u}{d\theta}$ is the coefficient of dilatation. This, under the conditions assumed, will, of course, be different according as the other stresses or other strains are maintained constant. In the case of a bar of india-rubber stretched by a variable weight, all the elements of stress but one vanish or are constant. If the stress be somewhat considerable it is found that $\frac{du}{d\theta}$ is negative. It follows that increase of weight will liberate heat in the india-rubber. But the same will not be true if the stretching weight be nil or very small, nor again if the periphery of the bar is held so that it cannot contract transversely as the weight extends it longitudinally, unless (which is improbable) it should be found that in these cases the coefficient of dilatation is negative.

APPENDIX II.

ON CAPILLARITY.

The equations obtained in Appendix I. may also be applied to the equilibrium of the surface film of a liquid in contact with its own vapour. This subject is generally known under the name of Capillarity, from its having first been studied in connection with Capillary tubes (Maxwell, *On Heat*, 1871, p. 263). Thus let the body considered be the film of fluid at the surface of a fluid, and let it be so small in volume that its capacity of heat in virtue of its volume may be neglected. Let T be the surface tension, and S the surface. Then T is a function of θ only: hence, from an equation analogous to Equation (3), Appendix I., we obtain

$$\frac{dT}{d\theta} \times \frac{dS}{d\phi} = -1,$$

or

$$\frac{dT}{d\theta} = -\frac{d\phi}{dS} = -\frac{1}{\theta}\frac{dq}{dS}$$

(by Equation (1), Appendix I.), where q is heat absorbed.

If then $\frac{dT}{d\theta}$ is negative, as is usually the case, extension of surface means absorption of heat.

The question of the equilibrium of vapour at a curved surface of liquid has been treated by Sir Wm. Thomson. The following is mainly taken from his paper (*Proc. Royal Society of Edinburgh*, 1870, Vol. VII., p. 63).

In a closed vessel containing only liquid and its vapour, all at one temperature, the liquid rests, with its free surface raised or depressed in capillary tubes and in the neighbourhood of the solid boundary, in permanent equilibrium according to the same law of relation between curvature and pressure as in vessels open to the air. The permanence of this equilibrium implies physical equilibrium between the liquid and the vapour in contact with it at all parts of its surface. But the pressure of the vapour at different levels differs according to hydrostatic law. Hence the pressure of saturated vapour in contact with a liquid differs according to the curvature of the bounding surface, being less when the liquid is concave, and greater when it is convex. And detached portions of the liquid in separate vessels, all enclosed in one containing vessel, cannot remain permanently with their free surfaces in any other relative positions than those they would occupy if there were hydrostatic communication of pressure between the portions of liquid in the several vessels. There must be evaporation from those surfaces which are too high, and condensation into the liquid at those surfaces which are too low—a process which goes on until hydrostratic equilibrium, as if with free communication of pressure from vessel to vessel, is attained. Thus, for example, if there are two large open vessels of water, one considerably above the other in level, and if the temperature of the surrounding matter is kept rigorously constant, the liquid in the higher vessel will gradually evaporate until it is all gone and condensed into the lower vessel. Or we may suppose a capillary tube, with a small quantity of liquid occupying it from its bottom up to a certain level, to be placed upright in the middle of a quantity of the same liquid with a wide free surface, and contained in a hermetically sealed exhausted receiver. The vapour will gradually become condensed into the liquid in the capillary tube, until the level of the liquid in it is the same as it would be were the lower end of the tube in hydrostatic communication with the large mass of liquid. The effect would be that in a very short time liquid would visibly rise in the capillary tube, and that, provided care were taken to maintain the equality of temperature all over the surface of the hermetically sealed vessel, the liquid in the capillary tube would soon take very nearly the same level as it would have were its lower end open; sinking to this level if the capillary tube were in the beginning filled too full, or rising to it if there is not enough of the liquid in it at first to fulfil the condition of equilibrium.

The following shews precisely the relations between curvatures, differences of level, and differences of pressure with which we are concerned.

Let p be the pressure of equilibrium above the curved surface in the tube, rr' the principal radii of curvature of that surface, and T the surface tension: then by the principles of Capillarity the upward drag on the surface, due to the tension, is $T\left(\frac{1}{r}+\frac{1}{r'}\right)$. Hence the pressure within the liquid, immediately below the surface is

$$p-T\left(\frac{1}{r}+\frac{1}{r'}\right).$$

Let π be the equilibrium pressure of the vapour at the plane surface of the liquid, ρ the density of the liquid, σ the density of the vapour, h the height at which the liquid stands in the tube above the plane surface: then clearly

$$\pi = \left[p - T\left(\frac{1}{r} + \frac{1}{r'}\right)\right] + h\rho \text{ ....(1).}$$

But also

$$\pi = p + h\sigma \text{ ....(2).}$$

Therefore

$$\pi(\rho - \sigma) = p(\rho - \sigma) + T\left(\frac{1}{r} + \frac{1}{r'}\right)\sigma,$$

or

$$p = \pi - \frac{T\sigma}{\rho - \sigma}\left(\frac{1}{r} + \frac{1}{r'}\right) \text{..................(3),}$$

which gives the relation between the pressure of equilibrium above the curved surface and that above the plane surface.

In strictness the value of σ to be used ought to be the mean density of a vertical column of vapour extending through the given height. But in all cases in which we can practically apply the formulæ, according to our present knowledge of the properties of matter, the difference of densities in this column is very small, and may be neglected. Hence, if H denote the height above the plane surface of the liquid of an imaginary homogeneous fluid which, if of the same density as the vapour at that plane, would produce by its weight the actual pressure π, we have

$$\sigma = \frac{\pi}{H}.$$

But by Equations (1) and (2)

$$(\rho - \sigma)h = T\left(\frac{1}{r} + \frac{1}{r'}\right);$$

hence by Equation (3)

$$\pi - \sigma h = \pi\left(1 - \frac{h}{H}\right).$$

For vapour at ordinary atmospheric temperatures, H is about 1,300,000 centimetres. Hence in the capillary tube which would keep water up to a height of 13 metres above the plane level, the curved surface of the water is in equilibrium with the vapour in contact with it, when the pressure of the vapour is less by about $\frac{1}{1000}$th of its own amount than the pressure of vapour in equilibrium at a plane surface of water at the same temperature.

APPENDIX III.

ON THE CONTINUITY OF THE LIQUID AND GASEOUS STATES OF MATTER.

The chapters on Fusion and Vaporization will be rendered more complete by a brief account of Dr Andrews' important researches on the continuity between the liquid and gaseous states of matter. This account is mainly taken, by permission of Messrs Longmans, from the late Prof. Maxwell's work on *The Theory of Heat*, 1877, Ch. VI.

In Fig. 1 the full lines represent certain Isothermal lines for Carbonic Acid Gas (CO_2), i.e. curves produced by making it vary in pressure and volume, while the temperature is kept constant at the value written (in degrees Cent.) along each line. The ordinates represent pressures in atmospheres, and the abscissæ represent volumes. The variation is supposed to be produced by diminishing the volume, e.g. the gas may be supposed to be contained in a cylinder, the piston of which is gradually lowered.

Take one of these isothermals, e.g. that at 21°·5. Beginning from the right hand, we have first a curved line *AB*. During this part of the compression, the substance is entirely in the state of a gas. As the volume diminishes the pressure increases, and the result is a regular curve, which if the gas were perfect, or *pv* constant, would be an equilateral hyperbola. At the point *B*, corresponding to about 60 atm., the gas commences to liquefy. From this point the decrease of volume produces no increase of pressure, but simply liquefies more and more of the gas. The curve becomes therefore a horizontal straight line *BC*. At the point *C* the whole of the gas is liquefied. From this point any further reduction of volume is resisted by the elastic force of the liquid, which is very great; and the isothermal line therefore rises in the almost vertical curve *CD*.

Now the length of the horizontal part *BC*, during which the gas is partly in the liquid, partly in the gaseous state, is not the same for different temperatures. For 13°·1 its length is seen to be *EF*, which is much greater than *BC*; while for temperatures above

21°·5 it is found to be shorter than *BC*. The dotted line *DBECF* is the boundary of all these horizontal lines, up to a certain point *G*, corresponding to 30°·92, at which their length vanishes. In other words, at temperatures above 30°·92 the "gas line" *AB*, and the

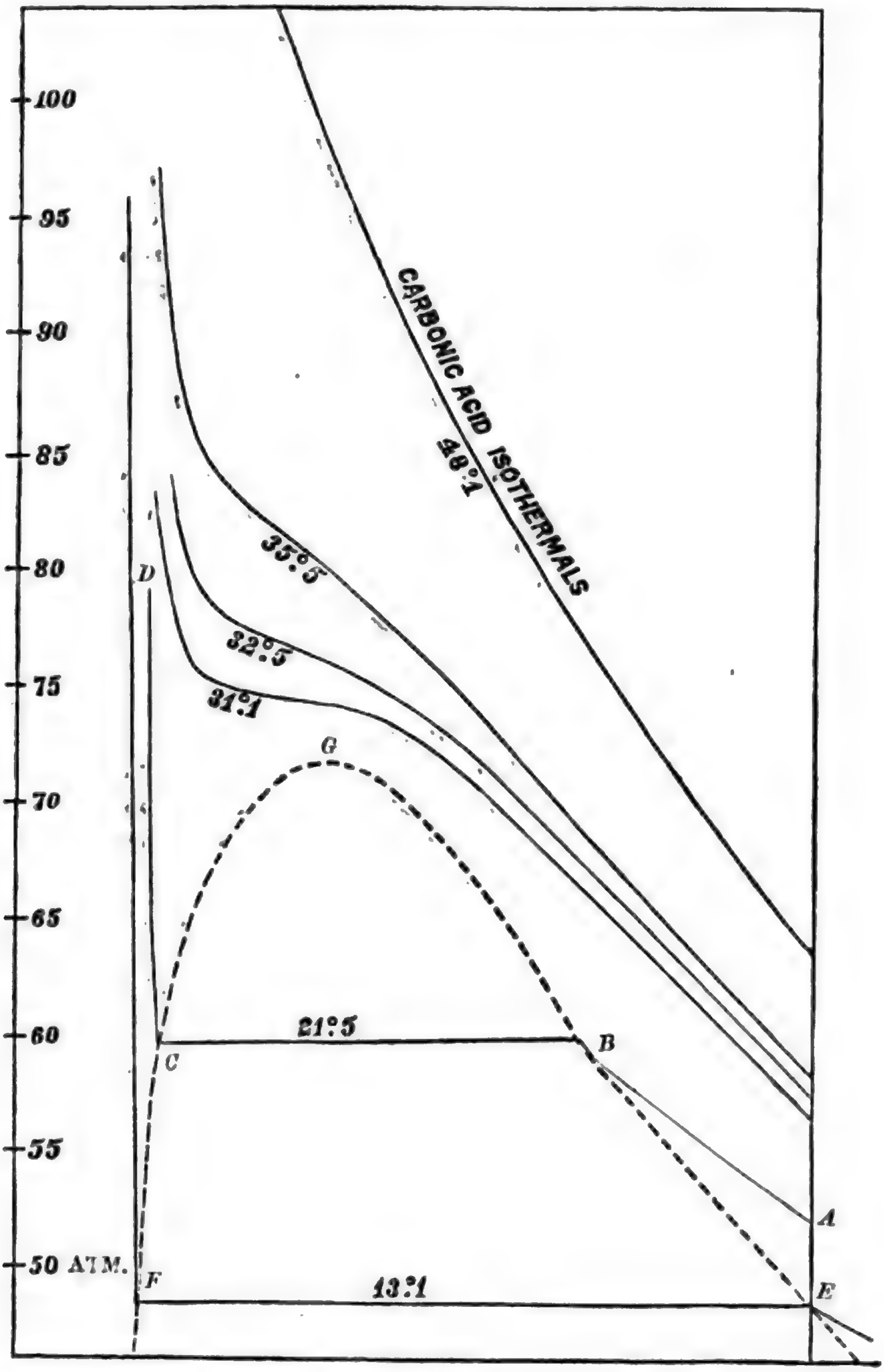

Fig. 1.

"liquid line" *CD* meet each other, without any intervening portion.

In the case of steam, for which such isothermal lines were first drawn, similar phenomena occur; and when it was seen that the gas line and the liquid line thus continually approached each other as the temperature was raised, the question naturally arose, Do they ever meet? If they do meet, then at that temperature the substance cannot exist partly as a liquid and partly as a vapour, but must be entirely converted, at the corresponding pressure, from the state of liquid to that of vapour; or else, since in this case the vapour and liquid have the same density, it may be suspected that the distinction between liquid and vapour has here lost its meaning.

The answer to this question has been to a great extent supplied by a series of very interesting researches.

In 1822 M. Cagniard de la Tour[1] observed the effect of a high temperature upon liquids enclosed in glass tubes of a capacity not much greater than that of the liquid itself. He found that when the temperature was raised to a certain point, the substance, which till then was partly liquid and partly gaseous, suddenly became uniform in appearance throughout, without any visible surface of separation, or any evidence that the substance in the tube was partly in one state and partly in another.

He concluded that at this temperature the whole became gaseous. The true conclusion, as Dr Andrews has shewn, is that the properties of the liquid and those of the vapour continually approach to similarity, and that, above a certain temperature, the properties of the liquid are not separated from those of the vapour by any apparent distinction between them.

In 1823, the year following the researches of Cagniard de la Tour, Faraday succeeded in liquefying several bodies hitherto known only in the gaseous form, by pressure alone, and in 1826 he greatly extended our knowledge of the effects of temperature and pressure on gases. He considers that above a certain temperature, which, in the language of Dr Andrews, we may call the critical temperature for the substance, no amount of pressure will produce the phenomenon which we call condensation, and he supposes that the temperature of 166° F. below zero is probably above the critical temperature for oxygen, hydrogen, and nitrogen.

Dr Andrews has examined carbonic acid under varied conditions of temperature and pressure, in order to ascertain the relations of the liquid and gaseous states, and has arrived at the conclusion that the gaseous and liquid states are only widely

[1] *Annales de Chimie*, 2nd Series, Vols. xxi. and xxii.

separated forms of the same condition of matter, and may be made to pass one into the other without any interruption or breach of continuity[1].

The diagram, Fig. 1, for carbonic acid is taken from Dr Andrews' paper, with the exception of the dotted line shewing the region within which the substance can exist as a liquid in presence of its vapour. The base line of the diagram corresponds, not to zero pressure, but to a pressure of 47 atmospheres.

The lowest of the isothermal lines is that of 13°·1 C. or 55°·6 F.

This line shews that at a pressure of about 47 atmospheres condensation occurs. The substance is seen to become separated into two distinct portions, the upper portion being in the state of vapour or gas, and the lower in the state of liquid. The upper surface of the liquid can be distinctly seen, and where this surface is close to the sides of the glass containing the substance it is seen to be curved, as the surface of water is in small tubes.

As the volume is diminished, more of the substance is liquefied, till at last the whole is compressed into the liquid form.

Liquid carbonic acid, as was first observed by Thilorier, dilates as the temperature rises to a greater degree than even a gas, and, as Dr Andrews has shewn, it yields to pressure much more than any ordinary liquid. From Dr Andrews' experiments it also appears that its compressibility diminishes as the pressure increases. These results are apparent even in the diagram. It is, therefore, far more compressible than any ordinary liquid, and it appears from the experiments of Andrews that its compressibility diminishes as the volume is reduced.

It appears, therefore, that the behaviour of liquid carbonic acid under the action of heat and pressure is very different from that of ordinary liquids, and in some respects approaches to that of a gas.

If we examine the next of the isothermals of the diagram, that for 21°·5 C. or 70°·7 F., the approximation between the liquid and the gaseous states is still more apparent. Here condensation takes place at about 60 atmospheres of pressure, and the liquid occupies nearly a third of the volume of the gas. The exceedingly dense gas is approaching in its properties to the exceedingly light liquid. Still there is a distinct separation between the gaseous and liquid states, though we are approaching the critical temperature. This critical temperature has been determined by Dr Andrews to be 30°·92 C. or 87°·7 F. At this temperature, and at a pressure of from 73 to 75 atmospheres, carbonic acid appears to be in the critical condition. No separation into liquid and vapour can be detected, but at the same time very small variations of pressure or of temperature produce such great variations of density that flickering movements are observed in the tube "resembling in an exaggerated form the appearances exhibited during the mixture of liquids of different densities, or when columns of heated air ascend through colder strata."

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[1] *Phil. Trans.* 1869, p. 575.

The isothermal line for 31°·1 C. or 88° F. passes above this critical point. During the whole compression the substance is never in two distinct conditions in different parts of the tube. When the pressure is less than 73 atmospheres the isothermal line, though greatly flatter than that of a perfect gas, resembles it in general features. From 73 to 75 atmospheres the volume diminishes very rapidly, but by no means suddenly, and above this pressure the volume diminishes more gradually than in the case of a perfect gas, but still more rapidly than in most liquids.

In the isothermals for 32°·5 C. or 90°·5 F. and for 35°·5 C. or 95°·9 F. we can still observe a slight increase of compressibility near the same part of the diagram, but in the isothermal line for 48°·1 C. or 118°·6 F. the curve is concave upwards throughout its whole course, and differs from the corresponding isothermal line for a perfect gas only by being somewhat flatter, shewing that for all ordinary pressures the volume is somewhat less than that assigned by Boyle's law.

Still at the temperature of 118°·6 F. carbonic acid has all the properties of a gas, and the effects of heat and pressure on it differ from their effects on a perfect gas only by quantities requiring careful experiments to detect them.

We have no reason to believe that any phenomenon similar to condensation would occur, however great a pressure were applied to carbonic acid at this temperature.

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